TIN

ITS MINING, PRODUCTION, TECHNOLOGY, AND APPLICATIONS

BY

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Member, American Institute of Mining and Metallurgical Engineers,
American Institute of Chemical Engineers

American Chemical Society
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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the pioduction and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development The American Chemical Society named as Trustees, to make the necessary ariangements for the publication of the monographs, Charles L Parsons, Secretary of the American Chemical Society, Washington, D C , John E Teeple, Treasurer of the American Chemical Society, New York City, and Professor Gellert Alleman of Swarthmore College The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

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The development of knowledge in all branches of science, a especially in chemistry, has been so rapid during the last fif years and the fields covered by this development have been varied that it is difficult for any individual to keep in touch wi the progress in branches of science outside his own specialt In spite of the facilities for the examination of the literatu given by Chemical Abstracts and such compendia as Beilstein Handbuch der Organischen Chemie, Richter's Lexikon, Ostwal(Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut Handbuch der Anorganischen Chemie and the English ar French Dictionaries of Chemistry, it often takes a great de of time to coordinate the knowledge available upon a single topi Consequently when men who have spent years in the study (important subjects are willing to coordinate their knowledg and present it in concise, readable form, they perform a servic of the highest value to their fellow chemists

It was with a clear recognition of the usefulness of reviews (this character that a Committee of the American Chemica Society recommended the publication of the two series of mono graphs under the auspices of the Society

Two rather distinct purposes are to be served by these mono graphs   The first purpose, whose fulfilment will probably rende to chemists in general the most important service, is to presen the knowledge available upon the chosen topic in a readabl form, intelligible to those whose activities may be along a wholl different line   Many chemists fail to realize how closely thei investigations may be connected with other work which on th surface appears far afield from their own   These monograph will enable such men to form closer contact with the work o chemists in other lines of research   The second purpose is to promote research in the branch of science covered by the mono graph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions i which investigation needs to be extended   To facilitate the attainment of this purpose, it is intended to include extendec references to the literature, which will enable anyone interestec to follow up the subject in more detail   If the literature is sc voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations The success of the venture will depend in large part upon the measure of cooperation which can be secured in the preparation of books dealing adequately with topics of general interest, it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it

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THIS VOLUME IS RESPECTFULLY DEDICATED TO
COLIN GARFIELD FINK, PROFESSOR OF CHEM-
ICAL ENGINEERING, COLUMBIA UNIVERSITY, TO
WHOM THE AUTHOR OWES HIS FIRST INTEREST
IN THE SUBJECT, AND TO WHOM HE IS GREATLY
INDEBTED FOR HELP, ADVICE, AND CONSTANT
ENCOURAGEMENT DURING THE LAST SIX YEARS

PREFACE

In this monograph the author has attempted to cover the subject of tin in a somewhat comprehensive manner The history, the physical and chemical properties, and the pioduction, distribution, and consumption of the metal have been treated The ores and ore deposits, the ore dressing, mining, smelting, refining, and metalluigy represent the distinctly metallurgical sections These have been treated somewhat from the viewpoint of the metallurgical chemist iather than from the viewpoint of the mining engineer The industrial applications of tin in its simpler forms, as in plating, hot-dipped coatings, foil, and collapsible tubes, are written fiom the viewpoint rather of the chemist than of the mechanical engineer The section on alloys has been written from the standpoint of the physical metallurgist, and the sections on corrosion from that of the chemical engineer The chapter on compounds is distinctly chemical An attempt has been made to gather together the large amount of information, examine the material critically, and present it in usable form The section on secondary tin has been written from the economic as well as the metallurgical and chemical side The same holds true for detinning of tin-plate scrap Much of the important data on tin, in the phases either of its production or of its consumption, has been widely spread This volume is an attempt to gather together as much as possible of the authoritative available information for the use of those in the various fields in which tin finds application

The author has made free use of a number of references of an authoritative nature pertaining to the various phases of the production of tin from its ores, its smelting, and its commercial applications Consideiable information in reference to ores and ore deposits has been obtained from Jones' "Tinfields of the World", on ore dressing from Taggart's "Handbook of Ore Dressing", on alloys from the International Critical Tables and the data sheets of the American Society of Steel Treating, on compounds from Mellor's "Treatise of Inorganic and Theoretical Chemistry", and on corrosion from the corrosion bibliography of the National Research Council

The author wishes to acknowledge his indebtedness to a numbei of men and organizations actively engaged either in the tin industries or in other businesses closely connected with the production or con-

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sumption of tin metal Chief among these are E K Browne of tl
American Metal Market of New York, for aid in connection with dai
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It is hoped that this volume may be somewhat useful as a refere
and as a stimulant to those engaged in the mining, milling, smelti
refining, and alloy founding of tin metal, and to others interested
the manifold applications of tin in industry, in the form either of m
or of its compounds Criticism will be welcomed at all times and gr.
fully received The author will be only too glad to be the recipient
suggestions in connection with the production and use of this import
metal in our national economy

<div style="text-align: right">C L MANTELL</div>

Pratt Institute,
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TIN

CHAPTER 1

HISTORY

Tin, a component of bronze, was used as a metal prior to the dawn of history It does not follow, however, that prehistoric bronzes were made of metallic tin Tin does not occui "native" to any extent, although grains of metallic tin occur as a subordinate admixture in some of the gold mines of Siberia, Guiana, and Bolivia When the unalloyed metal was first introduced can not be definitely ascertained It is generally believed that tin was employed in the arts in the Grecian age of Homer and the Biblical times of Moses The metal and some of its alloys were known to Hiram of Tyre and his artificers connected with the building of King Solomon's temple It is very likely that an early barbarian discovered tin when he attempted to put out or bank his fire with handfuls of black alluvial sand Perhaps at one time he employed alluvial cassiterite and found, to his surprise the next morning, particles of a bright, shiny new metal

The most primitive method of smelting tin was that in use in the Bronze Age The early artificers required the metal to enable them to mix it in varying proportions with copper to make different kinds of weapons and to harden the copper Socketed axes required 4 to 13 per cent tin, and spear and lance heads 11 to 16 per cent Gowland came to the conclusion, as a result of a number of analyses of ancient bronze weapons, that the varying tin content was not due merely to chance but to the skill of the smiths of the later Bronze Age It is thought that the smelting was carried out in trenches lined with clay and filled with brushwood Above this, small logs of wood were piled The mass was lighted and as soon as the logs were burning fiercely and the trench full of glowing embers, small quantities of tinstone were thrown upon the fire from time to time More wood and mineral were added until the required amount of tin had accumulated in the trench The fire was then allowed to die down or was raked away, and the molten metal ladled into a hole in the ground or into a clay mold near the furnace It is quite likely that later developments caused the use of a deep hole instead of a shallow pit to confine the fire Primitive blowers or bellows were introduced and the blast no longer admitted over the edge of the

cavity but through an opening just above the base of the furnace which was excavated near the edge of a bank of earth Molten tin was allowed to flow out through a tap hole at a point lower than the blast entrance Further progress was made in later years by erecting small cylindrical furnaces built of clay The operation of these was more convenient Most native furnaces are developments along the lines stated

Tin metal was not found native by the ancients They could have obtained it only by extraction from its ores In alluvial deposits the ore is found near or on the surface, and it gives up its metal more readily than the ores of most metals The early Britons were acquainted with the slagging operations involved in tin smelting, for many ancient slag hearths are found in Cornwall

Tin ore occurs in commercial quantities in only a few counties of the world These were not readily accessible to the Romans or Greeks until after the Cæsarian conquest of Britain It appears probable that the metal was scarce and costly Although more durable than lead or copper, vessels of tin are rarely found among the Greek or Roman antiquities, under conditions where vessels of lead and copper are comparatively common Articles of tin alloys, however, are often found

Moses, in the book of Numbers of the Bible, includes tin in his list of the metals then known The Hebrew word *bedil* was translated *cassiteros* in the Greek versions, and *stannum* in Latin translations In his *Historia Naturalis,* Pliny regarded tin as a variety of lead He states

> There are two kinds of *plumbum—nigrum* and *candidum* or *album* (*i e* black lead and shining or white lead) The *plumbum candidum* is the most valuable, and it was called *cassiteros* by the Greeks There is a fabulous story told of their going in quest of it to the islands in the Atlantic Ocean, and of its being brought in boats made of osiers covered with hides The *plumbum candidum* occurs as a black sand found on the surface of the earth, and is to be detected only by its weight, it is mingled with small pebbles, particularly in the dried beds of rivers The miners wash the sand, which is then melted in the furnace and becomes converted into *plumbum album*

Pliny's *plumbum candidum* was no doubt tin, just as his *plumbum nigrum* was lead Pliny described Roman vessels made of copper and coated with *stannum,* and stated that *plumbum candidum* was esteemed in the days even of the Trojan war Homer writes of it under the name *cassiteros*

The history of tin among the ancient peoples may be divided into the period corresponding to the exploitation of tin in Asia, and into a second period corresponding to the importation of the metal from Great Britain by the Phœnicians Articles of copper and copper alloys found in Mesopotamia belonging to the period of 4000 B C, upon analysis show that tin was not used in their manufacture The analysis

of an Egyptian bronze mirror belonging to the period of 1600 B C, showed that tin was present Bronze seems to have been an Oriental discovery Tin was used by the Egyptians in 700-600 B C, as proved by the finding of a strip of tin free from lead and silver in the wrappings of an Egyptian mummy of an age not later than 600 B C The Chinese bronze industry flourished in 1800-1500 B C, so that tin must have been known in China at that time The present-day Oriental custom of making coffin lace by the laborious method of hand beating tin into tinfoil, which is to be cut into decorative forms, has its origin in the dim and distant past before the Christian era

References to the tin trade of the Phœnicians, the Greeks, the Gauls and the Romans are very scanty Herodotus states that he was not acquainted with the Cassiterides Islands from whence came our tin In his *De Bello Gallico,* Cæsar talks of the tin trade, as did Aristotle in his *De Mirabilibus Auscultationibus,* and Strabo in his *Geographica* Pliny's fabulous story could very well refer to the transport of tin or tin ore from the Scilly Islands and Cornwall by vessels resembling the coracles of the ancient Britons About 1000 B C the Phœnicians appear to have worked tin mines in Cornwall, ages before the Roman conquest They seem to have conveyed there a body of colonists who established an emporium The metal was also obtained from the inhabitants by barter They called the Scilly Islands and the shores of Cornwall the Cassiterides, and Dionysius, writing in the beginning of the fourth century, called them Hesperides In the Bible, Ezekiel refers to the tin commerce of the Phœnicians at Tyre

The early Greek alchemists called tin Hermes, but about 500 A D the alchemists called it Zeus or Jupiter, and represented it by the symbol ♃, which was understood to mean the thunderbolts of the king of the gods Because tin forms brittle alloys with many metals, it was called *diabolus metallorum*—the devil of the metals The Latin Geber, in his *Summa Perfectionis Magisterii,* probably written about the twelfth century, said

> I intimate to the sons of learning that tin is a metallic substance which is white, but not pure white, it has a little ring, and emits a creaking sound, it partakes of a little earthiness, and possesses in its root both hardness and softness, it melts rapidly without catching fire, it does not take cupellation—*cineritium et cementum non exspectans,* and it is extensible when hammered Its vice is that, when alloyed, it makes every metallic body brittle excepting Saturn and pure Sol

The Spanish tin mines appear to have been abandoned under the government of the Moors. Much of the world's supply of tin about the thirteenth century came from Cornwall, although the tin mines of Saxony and Bohemia were probably discovered about that time The

Malay States and the East Indies are mentioned as sources of tin by Arabian writers of the eighth and ninth centuries A number of sixteenth century authors mentioned East Indian and Malacca tin, and many mines at Banka were estimated to have been worked by the Chinese before the seventeenth century Definite documentary history of the Cornwall mines does not begin earlier than 1156

The earliest tin-dressing and smelting operations were applied to alluvial tin deposits Polwhele, the historian, says "The stream tin from St Austell Moor is of the very purest kind Without any other management than being washed on the spot, it brings thirteen parts for twenty at the smelting house" Another early reference mentions the Regis tinstones, from which the metal was obtained after direct heating, the poorer stones being broken up and washed before smelting Evidences of these early preparations for smelting are still to be found in Looe Pool Valley, where boulders of hard rock show deep holes in which the tinstone was pounded Similar indentations of rock and the remains of a crude buddle or washing place have been discovered in the Islands of Scilly Improvements such as the stamp battery were introduced from the Continent early in the sixteenth century Prior to 1602 tinstone was crushed dry, but about that time a water-wheel-driven wet-stamp battery appears to have been employed A labor-saving stamping mill enters the records of 1671, and with it a shallow trench used to divide the product, evidently according to the rate of fall in water This operation was termed "trambling" or "buddling" About this time we also hear of calcination in a square kiln About 1742 only one steam engine was to be found in all Cornwall, but after that time progress was extremely rapid Stream works were giving way in importance to mine works, and the nineteenth century provided more efficient and automatic mechanisms for dressing with steam power, as well as heavier stamps, stone breakers, classifiers, self-acting calciners and the like

Pryce has classified the ores of Cornish tin as "shode, stream or mine," the term "shode" apparently referring to lump or gravel-size ore, between mine ore and stream tin in size and situation Early documentary references, however, describe the specific nature of a tin working as a "moor" or "stream" work

The highest output of tin concentrate on record in the year 1337 is given as 1,328 thousandweight, or about 600 tons, after which the Great Plague ruined the stannaries for some time Such events as the Wars of the Roses, which exerted an adverse effect for a long period, are held partially responsible for the fluctuation in tin output The

advance from 700 tons in the early part of the seventeenth century to 1,500 tons at the end was no doubt caused by the general use of the stamp battery introduced in the sixteenth century During the half century ending 1800, the output varied from 2,000 to 3,500 tons annually

CHAPTER 2

PHYSICAL AND CHEMICAL PROPERTIES OF THE METAL

Although so common and well known, tin is really a less abundant element than many of those less familiar and usually ranked with the scarce or rare elements such as cerium, yttrium, lithium, beryllium, titanium, zirconium, and vanadium

The color of tin is white, with a slightly bluish tinge When it is compared with nickel, the latter metal is brown in comparison, and with chromium, this substance is definitely blue Tin is whiter than silver or zinc Exceedingly thin films of tin transmit various shades of brown when light is caused to pass through the film The metal has a brilliant luster, and when highly polished has high light reflectivity The luster depends to a large extent upon the temperature at which the metal is poured when cast If the temperature be too high, iridescent colors may show on the surface as the result of oxide films If the pouring temperature be too low, the surface is dull Small amounts of foreign metals such as lead, arsenic, antimony, and iron decrease the luster of tin and impart a yellowish tinge to the metal

The structure is decidedly crystalline The cast metal is a mass of crystals. When a bar of tin is bent, it emits a characteristic creaking sound called the "cry" of tin, resulting from the grinding of the crystals one against the other during the bending of the metal Tin metal may lose its crystalline structure by cold working, but grain growth occurs rapidly under the influence of heat Metal which has been cast at a low temperature may become amorphous as the result of mechanical work, but if the material be heated below its melting point, say at 110° for a half hour or for a few minutes at 150°, recrystallization occurs If the surface of tinned plate, tin foil, or tin metal in cast form be etched with hydrochloric acid containing a little free chlorine, or with a solution of stannous chloride, attack occurs at the intercrystalline faces The surface shows patterns resembling the frost flowers on windowpanes in winter The etched appearance is called *moiré metallique* Fine dendritic surface crystals of tin may be obtained by casting the metal on a surface of polished steel In tin plate the intercrystalline boundaries are shown by fine grooves or channels, which result from the method of manufacture, during which the plates are drawn from

a bath of molten tin and allowed to drain More fusible impurities are forced, by the crystallization of the tin, to the intercrystalline junctions, after which the still fluid impurities drain off, leaving minute channels The fine grain structure obtained by quenching molten tin in water is not affected by annealings over long periods at temperatures below the melting point If, however, so-called "block tin" have its crystalline structure extremely subdivided by severe compression or working, it can be caused to recrystallize at 150° Tin crystals sometimes show lines which are due to stresses set up during rapid growth

Cold-rolled tin shows a tendency to recrystallize at ordinary temperatures immediately after rolling If annealing be carried out at 170° to 180°, secondary recrystallization occurs In this case the smaller crystals grow at the expense of their neighbors The resultant metal has a very coarse crystalline structure If rolled once again and allowed to stand, the primary crystals which form are larger than before, but about the same size as those produced by annealing at temperatures up to 150°

Single crystals of tin have been made by a number of investigators Mark[1] and his coworkers found that when a tin crystal is elongated to a wire and heated at 150° for three minutes, the wire is disrupted by recrystallization which begins at the ends, growing at the rate of approximately 1 millimeter per second The orientation of the new crystal in reference to the old one is such that the width of the wire is not changed on elongation Tammann and Mansuri[2] state that coalescence of the grains of powdered tin occurs by recrystallization at 142°

The physical properties of tin are given in Table 1

TABLE 1

PHYSICAL PROPERTIES OF TIN

		Authority
Absorption coefficient for β-rays (M)	M/D = 9 46	Crowther
Absorption coefficient for γ-rays (M) from		
Radium	M/D = 0 281	
Uranium	M/D = 0 341	
Thorium-D	M/D = 0 236	
Mesothorium	M/D = 0 305	Russell and Soddy
Atomic entropy at 25° C	11 17 Cal per degree	Lewis, Gibson and Latimer
Gray tin at 25° C	9 23 Cal per degree	Lewis, Gibson and Latimer
Atomic heat		
— 85° C	5 91	Schmitz
60° C	6 57	Schmitz
— 196° to — 253° C	3 41	Dewar[5]

[1] Mark, Polanyi, and Schmid, *Naturwiss*, 11 256 (1923), *Z Physik*, 32 684 (1925)
[2] *Z anorg Chem*, 126 119 (1923)

TABLE 1—*Continued*

		Authority
White tin at		
22 4° K	1 27	Lange
56 7° K	4 06	
101 1° K	5 40	
286 3° K	6 27	
Gray tin at		
15 5° K	0 599	Lange
31 5° K	1 675	"
92 5° K	4 42	"
283 7° K	6 13	"
Atomic heat of fusion	1712 Cals	Richards ·
Atomic radius	1 40 A	Pease [8]
Atomic refraction	18 6–27 0	Gladstone
Average compressibility		
β at 20°	1 9 × 10⁻⁶ per mega-bar at 300 mega-bars pressure	Richards [10]
	1 89 × 10⁻⁶ at atmospheric pressure	Adams, Williamson and Johnston [11]
	1 64 × 10⁻⁶ at 10,000 megabars pressure	Adams, Williamson and Johnston [11]
Boiling point	2440° C	Van Laar [12]
	2270° C	Greenwood [13]
	2270° C	Mott [14]
Capillary constant		
a^2 at 226° C	17 87 sq mm	Siedentopf [15]
247° C	15 74 sq mm	Hagemann [16]
346° C	15 77 sq mm	Hagemann
398° C	15 83 sq mm	Hagemann
Critical pressure	650 atmospheres	Van Laar [12]
Critical temperature	3730° C	Van Laar [12]
Cubic expansion		
Metal near melting point	0 0₃114	Vincentini and Omodei [17]
Liquid near melting point	0 0₄689	Vincentini and Omodei [17]
400° to 700° C, $d_4 = 6$ 97	0 0₄105	Bornemann and Siebe [18]
232° to 396° C, $d_4 = 7$ 01	0 0₄106	Hogness [19]
232° to 988° C, $d_4 = 6$ 98	0 0₄126	Omodei [20]
232° to 1600° C, $d_4 = 6$ 98	0 0₄100	Day, Sosman and Hostetter [21]
232° to 1600° C, $d_4 = 6$ 99	0 0₄114	Vincentini and Omodei [22]
Cubic expansion		
9° to 72° C	0 0₄7	Kopp [23]
Diffusion coefficient (k) per sq cm/day		
Sn into Hg at 10 7° C	1 53	Von Wogau [24]
Sn into Au at 500° C	4 65	Roberts-Austen [25]
Pb in Sn at 500° C	3 18	Roberts-Austen [25]
Elastic limit	0 1 ton per sq in	Coe [26]
Elastic modulus	4148 kgrms per sq mm	Wertheim [27]
Observed value	4170 kgrms per sq mm	Stuart [28]
Calculated value	4130 kgrms per sq mm	Stuart [28]
Electrical conductivity		
Ag = 100	14 01	Becquerel [29]
At −183° C	294,000 mhos	Dickson [30]
− 78° C	114,000 mhos	"
0° C	76,600 mhos	"

TABLE 1—*Continued*

		Authority
Electrical conductivity		
91 45° C	54,800 mhos	Dickson [30]
176° C	42,300 mhos	"
Solid at melting point	44,900 mhos	Vassura [31]
Liquid at melting point	21,100 mhos	Vassura [31]
358° C	19,800 mhos	Muller [32]
860° C	15,400 mhos	Muller
Electrical resistance (micro-ohms per cubic centimeter)		
225° C	22 00	
Just before fusion	22 00	
Just after fusion	47 40	
300° C	49 44	Northrup and Suydam [33]
400° C	52 00	
500° C	54 62	
600° C	57 22	
700° C	59 88	
750° C	61 22	Northrup and Suydam [32]
Solid at melting point	21 7	Schulze [34]
Liquid at melting point	47 8	Schulze
Emissivity—		
Radiating capacity, tinned sheet iron (50° C)	0 04	
Tin, bright (50° C)	0 04	
Hardness on		
Von Moh Scale	1 8	Rydberg [35]
Brinell Scale at		
17° C	40 2	Sauerwald and Knehaus [36]
67° C	33 5	" " "
117° C	27 5	" " "
166° C	21 4	" " "
216° C	16 6	" " "
226° C	15 2	" " "
231° C	14 3	" " "
Cast	5 2	Coe [36]
Annealed at 100° C	5 0	Coe [36]
Heat of fusion	14 252 Cals	Person [37]
	6 67 kilo-joule per gram atom	Glaser [38]
		Awbery and Griffiths [39]
Heat of recrystallization		
For 50 per cent deformation	6 5 Cal	Van Liempt [40]
For 100 per cent deformation	13 0 Cal	Van Liempt [40]
Heat of vaporization	85 55 Cal	Van Liempt [41]
Internal pressures	68,700 megabars, or 10^8 dynes per sq cm	Traube [42]
Linear expansion coefficient		
0° to 100° C	0 0,2296	Matthiessen [43]
99 9 per cent Sn		
— 163° to 18° C	0 0,16	Cohen and Olie [44]
White tin		
10° to 90° C	0 0,209	Fizeau [45]
20° to 232° C	0 0,23 to 0 0,24	Cohen and Olie [44]
		Vincentini and Omodei [22]
Gray tin — 163° to 18° C	0 0,53	Cohen and Olie [44]
Single crystals		
∥ 20° C	0 0,305	Bridgman [46]
⊥ 20° C	0 0,1545	Bridgman [46]

TABLE 1—*Continued*

		Authority
Maximum load in tension, annealed tin	1 31 tons	Coe [26]
Melting point	231 9° C	National Bureau of Standards, 1919
500 atmospheres pressure	232 26° C	Adams and Johnston [47]
750 atmospheres pressure	233 09° C	" " "
1000 atmospheres pressure	233 89° C	" " "
1490 atmospheres pressure	235 47° C	" " "
2000 atmospheres pressure	237 18° C	" " "
Plasticity number		
Copper = 49 3	3 5	Edwards and Herbert [48]
Poissan's ratio	0 33	
Pressure for critical plasticity,		
Cast tin	1 08 tons per sq in	Coe [26]
Annealed at 100° C	1 24 to 1 39 tons per sq in	Coe [26]
Reflecting power		
$\lambda = 1 0\ \mu$	54 per cent	
2 0 μ	61 per cent	
4 0 μ	72 per cent	
7 0 μ	81 per cent	Coblentz [49]
10 0 μ	84 per cent	
12 0 μ	85 per cent	Coblentz [49]
Refraction equivalent		
$(M-1)/D$	0 1686	Haagen [50]
Specific gravity		
White tin	7 2984[15°]	
Rhombic	6 53–6 56[1,°]	
Gray	5 8466[18°]	
Commercial	7 5	Lewis [51]
Molten 250° C	6 982	Day, Sosman, Hostetter [31]
300° C	6 943	" " "
500° C	6 814	" " "
700° C	6 695	" " "
900° C	6 578	" " "
1000° C	6 518	" " "
1200° C	6 399	" " "
1400° C	6 280	" " "
1600° C	6 162	" " "
Specific heat	0 0514	Dulong and Petit [52]
White tin at − 193° C	0 0390	Bronsted [53]
Gray tin at − 193° C	0 0319	Bronsted
20° to − 188° C	0 0502	Richards and Jackson [54]
− 196° to − 253° C	0 0286	Dewar [5]
0° to 100° C	0 055	Regnault [55]
Molten tin	0 0637	Spring [56]
250° to 350° C	0 0637	Person [57]
Specific refractory power	19 89	Haagen [50]
Specific volume		
20° C	0 1395	Hess [58]
409° C	0 1462	Bornemann and Siebe [12]
474° C	0 1473	" " "
523° C	0 1479	" " "
574° C	0 1486	" " "
602° C	0 1490	" " "
648° C	0 1499	" " "
Stopping power for α-rays	3 37	Bragg [50]

TABLE 1—*Continued*

		Authority
Surface tension	598 to 681 2 mgs per mm	Quincke [60]
300° C	526 dynes per cm	Hogness [19]
350° C	522 " " "	"
400° C	518 " " "	"
450° C	514 " " "	"
500° C	510 " " "	"
In vacuo at 247° C	539 8 " " "	Hagemann [16]
Tensile strength	1 ton per sq in	
Thermal conductivity		
Ag = 100	31 2	Despretz [61]
— 170° C	0 195 absolute units	Lees [62]
15° C	0 1528 " "	Kirchhoff and Hausemann [63]
0 C	0 1528 " "	Lorenz [64]
100° C	0 1423 " "	Lorenz
200° C	0 145 " "	Jakob [6J]
292° C	0 081 " "	Konno [66]
417° C	0 079 " "	"
498° C	0 078 " "	"
Torsion modulus		
0° to 20° C	109×10^6 grams per sq cm, to 157×10^6 grams per sq cm	Sutherland [67]
— 15° C	135×10^6	Sutherland [67]
Trouton's constant	34 34	Van Liempt [41]
Valency attraction	$\sqrt{A} = 38$	Van Laar [68]
Vapor pressure		
2005° C	126 mm Hg	Ruff and Mugdan [69]
2045° C	178 mm "	" " "
2160° C	372 mm "	" " "
2190° C	485 mm "	" " "
2195° C	502 mm "	" " "
2270° C	755 mm "	" " "
1970° C	101 mm "	Greenwood [70]
2100° C	262 mm "	"
2270° C	760 mm "	"
1010° C	10^{-4} mm "	Johnston [71]
Velocity of crystallization	90 mm per min	Czochralsky [72]
Velocity of sound through tin	2640 4 meters per sec	Masson [73]
Viscosity,		
n at 280° C	0 01678	Pluss [74]
296° C	0 01664	"
357° C	0 01421	"
389° C	0 0311	"
Volume change on fusion and solidification		
Per cent at 232° C	2 7	Bornemann and Siebe [18] Endo [75] Toepler [76]

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57. *Ann chim phys* (3) 21 295 (1847), (3), 24 136 (1848)
58 *Ber deut physik Ges*, 3 403 (1905)
59 *Proc Phys Soc*, 34 51 (1922), *Phil Mag* (6), 11 617 (1906)
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75 *J Inst Metals*, London, 30 121 (1923)
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Tin is one of the few metals which have sufficient dignity to be subject to a "disease" Many workers have observed that ordinary tin changes into a gray powder when exposed to extremes of cold Medallions, coins and antiques in museums acquire a surface crust of powdery gray tin which gradually grows, seemingly self-catalyzed until complete disintegration results This is the so-called "tin pest" or "disease" of the museums Krause[3] states that Aristotle[4] refers to the change tin undergoes when subjected to extreme temperatures Erdman[5] in 1851 noted structural changes in organ pipes He thought them to be the effect of vibration Fritzsche[6] described the disintegration of pig tin After exposure to the Russian winter of 1867-8, when the temperature during January fell as low as — 38° C, some blocks of Banka tin had disintegrated to granular crystalline pieces and coarse powder A large number of workers have noted the same effect Gowland[7] refers to the change in an old vessel, consisting of 94 35 per cent tin, 5 06 per cent lead, traces of iron and copper, 0 59 per cent oxygen and carbon dioxide, in the following words

The extraordinary molecular change which the metal of this vessel has undergone is of more interest to the physicist and metallurgist than to the antiquary The metal is not much oxidized, yet it is so exceedingly brittle that it can be easily broken with the fingers The effect of time upon it has resulted in a complete alteration of its molecular structure, the mass of the alloy being converted into an agglomeration of crystals, and to this its brittleness is due On smelting and casting a small fragment I found that the crystalline structure disappeared and the metal regained its original toughness

When tin or a tin alloy is affected by tin pest, gray colored spots appear and the metal becomes brittle Expansion occurs so that the product occupies a greater volume than the unaffected tin The expansion produces pustule-like or nodular excrescences at the affected points Transformation extends radially outward from the spots until the whole mass is infected The metal then rapidly breaks down to a brittle powder The disease is infectious and can be propagated by inoculation Transformation can be begun by contact between a grain of the powder and a piece of sound metal The metal becomes sick in an analogous manner to that of the human organism when attacked by pathogenic bacteria Once infected, the whole mass is in danger Powdery gray tin shows the same analysis as that of the ordinary white metal In other words, gray tin is an allotropic modification of the elemental metal E Cohen and C Van Eijk[8] show that tin pest is due to the

[3] *Prometheus*, 11 701 (1900)
[4] "De Mirabilibus Aucultationibus"
[5] *J Prakt Chem* (1), 52 428 (1851)
[6] *Mem Acad St Petersburg* (1), 7 15 (1870)
[7] *Archaeologia*, 56 13 (1899)
[8] *Versl Akad Amsterdam*, 8 36, 102 (1899), *Z Phys Chem*, 30 601 (1899)

enanthiomorphic change of ordinary white tetragonal tin into gray tin
If white tin be powdered, mixed with some gray tin, and kept at a low
temperature, say — 50° C, for a few days, the entire mass changes
to gray tin, and conversely, gray tin changes to white tin by warming
the mass on a water bath Measurements of the potential difference
of the two forms of tin in a cell with stannous chloride as electrolyte
give a zero value at 18° C ; at higher temperature the gray form is the
positive pole, and at lower temperature, the white The transition tem-
perature is 18° C Consequently,
when the ordinary metal is kept
below 18° C, it is metastable, and
before equilibrium can be reached,
it must change into the gray form
As Cohen and Inouye [9] expressed it,
white tin under ordinary conditions
is in a metastable state, but under
ordinary atmospheric conditions, the
change is exceedingly slow The rate
of change is accelerated by lowering
the temperature, reaching a max-
imum at about — 50°, and there-
after diminishes as illustrated by
Figure 1 Janecke [10] observed the
change through an extended interval of temperature about 20° and 600
atmospheres pressure Stepanoff [11] studied the rate of transformation
of gray and white tin

FIG 1 —Relative speeds of transforma-
tion of ordinary tin to gray tin at
different temperatures

Hasslinger [12] states that a tinned iron vessel showed a crystalline,
brittle surface after it had been kept at 16° to 45° C for two years He
inoculated other masses of tin with small portions of this crystalline
metal These were transformed in a similar manner, the affected area
increasing 3 to 5 mm in diameter daily No difference could be noted
between experiments at 7°, 19° and 37° C When tin foil was inocu-
lated, the change extended through the thickness of the foil The crys-
talline tin preserves its appearance up to near the melting point, but
becomes normal after melting and again solidifying E Cohen [13] showed
that the structural change of the worked metal consists in a recrystal-
lization process, the result of which is the formation of larger tin

[9] *Chem Weekbl*, 6 881 (1909)
[10] *Z phys Chem* 90 257, 313 (1915)
[11] *Ann Inst Phys Chem (Leningrad)*, 2 500 (1924)
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Elektrochem*, 18 616 (1912), 19 23 (1913), *Z phys Chem*, 33 57 (1900), 35 588 (1900),
36:513 (1901), 48 243 (1904), 63 625 (1908), 68 214 (1909)

crystals from smaller ones, and that the various forms of mechanically worked tin are in a metastable condition with reference to unstrained tetragonal tin above 18° C, and also with reference to gray tin below 18° C The so-called *moiré metallique,* which results when tin plate is etched by means of hydrochloric acid and potassium chlorate, corresponds with the recrystallized tin, and this can be used to start the change in other samples of tin plate

Bijl and Kolkmeijei [14] show from their X-ray studies of gray tin that it crystallizes in the cubic system Its space-lattice is of the diamond type with an edge of unit cube a $= 6\,46$ Å units

Tin exists in a number of allotropic forms, these are shown diagrammatically in Figure 2 At low temperatures the stable form is gray cubic, or *alpha* tin, which changes at 18° C to ordinary white tetragonal or *beta* tin This suffers transposition at 161° C to the so-called rhombic brittle, or *gamma* tin, which at 232° C passes into the molten state Von Simson [15] states that according to his X-ray studies, *gamma* tin is hexagonal

Tin metal is soft, it can be readily cut with a knife, but when filed it chokes the teeth of the tool On the von Moh scale it shows a hardness of 1 8 as compared to 1 5 for lead and 2 5 for gold The metal is slightly hardened by hammering The variation of the hardness of tin with temperature is discussed under the manufacture of tin foil (p 259)

Tin is most ductile in the neighborhood of 100° C, and at about 200° C it can be pulverized in a mortar Its tensile strength is low, being about 1 ton per square inch When bars of tin are subjected to repeated bending, heating of the metal occurs as the result of friction of the crystals
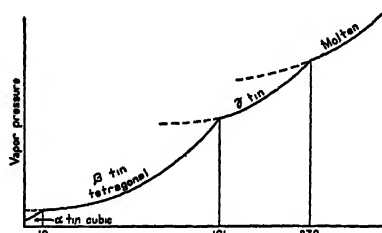

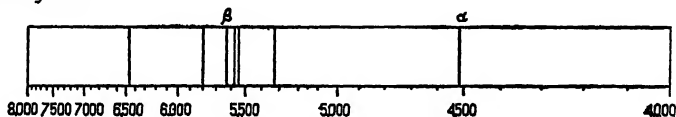FIG 2 —Equilibrium diagram of the allotropic forms of tin

FIG 3 —Spark spectrum of tin.

The most marked lines in the spark spectrum of tin, as shown in Figure 3, are the orange yellow line 6453, the yellow line 5799, the

[14] *Chem Weekbl*, 15 1264 (1918), *Proc Acad Amsterdam,* 21 405, 494, 501 (1919)
[15] *Z phys Chem* 109 183 (1924).

yellowish green 5632β, the green lines 5589, 5563, and 5331, and the indigo blue line 4525α The vapor of tin is not luminescent under the influence of cathode rays

The electrical conductivity of tin is about one-seventh that of silver The electrical resistance varies considerably with temperature The values are plotted in Figure 4, in micro-ohms per centimeter cube The resistance of tin decreases normally with falling temperature down to — 269 2° C, or 3 8° K, when the resistance suddenly becomes immeas-
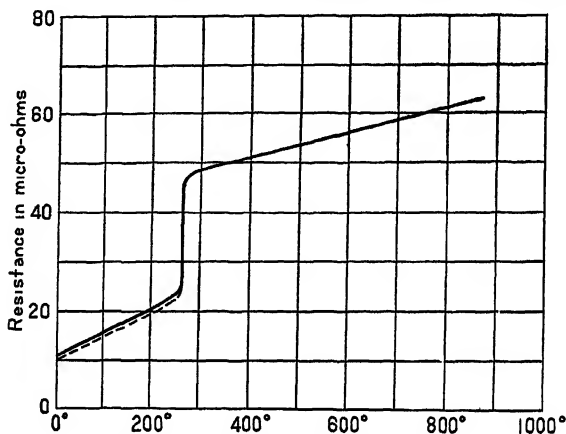

FIG 4—Electrical resistance of tin

urably small and the metal becomes an excellent conductor Tin shows marked volume changes during melting or freezing The dilatometer
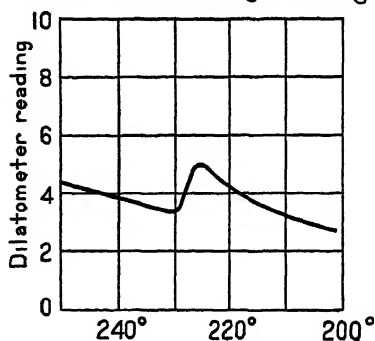

FIG 5—Volume change of tin during melting

readings of the volume change of tin during melting are plotted in Figure 5 Conversely, the specific volume of tin varies markedly with temperature, and the fluidity increases in an almost parallel line The change in volume in cc per kilogram of weight with increase in temperature is plotted in Figure 6 For those physical properties not specifically discussed, the reader is referred to the table of these properties (page 18)

Tin metal is not affected by hydrogen Considerable work in the literature seems to indicate the possibility of the occurrence of tin hydrides, but if they are formed, they are very readily decomposed

The metal is but little affected by air at ordinary temperatures, even in the presence of moisture, but gradually acquires a superficial tarnish Tammann [16] estimated that to form the first visible layer of oxide coating on tin metal in dry air would take 36×10^8 years Tin is readily
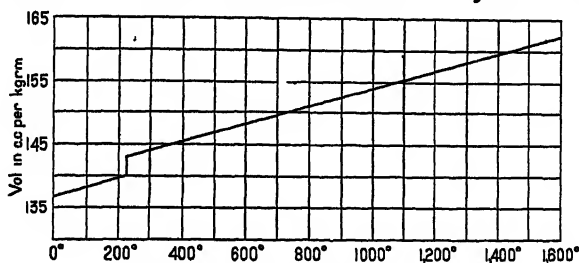

FIG 6 —Specific volume of tin

oxidized by air at elevated temperatures, with the formation of its oxides When the metal is heated to near its boiling point, it burns in air with a pale, white flame At ordinary temperatures it is appreciably affected by moist oxygen In this chapter we will attempt to confine ourselves to the purely chemical reactions of tin and discuss its corrosion in more detail elsewhere The halides unite directly with tin, forming stannic salts Dry chlorine reacts with tin at room temperatures (*See* Detinning) Fluorine does not react with tin at low temperatures, but at 100° it forms stannic fluoride Tin is feebly attacked by hydrofluoric acid, slowly dissolved by dilute hydrochloric and more rapidly by hot concentrated hydrochloric acid, with the formation of stannous chloride and the evolution of hydrogen The reaction is accelerated by the presence of small amounts of platinic chloride, or when tin is in contact with copper, antimony, silver, lead, or platinum metal Hot hydrobromic or hydriodic acid also readily dissolves tin Alkali hypochlorites react on tin, forming an oxychloride with the evolution of oxygen Chloric acid dissolves tin without the evolution of hydrogen, but with the formation of stannic chloride

Tin unites directly with sulfur when a mixture of the two elements is heated (*See* the tin sulfides) Hydrogen sulfide does not ordinarily act readily on tin at ordinary temperatures, but at 100° to 400° it forms stannous sulfide Over appreciable time periods, hydrogen sulfide tarnishes tin (*See* corrosion of tin plate by food products) Ammonium sulfide attacks tin more readily than does hydrogen sulfide When tin is fused with sodium sulfide, stannous sulfide is formed Sulfuryl chloride and sulfur monochloride, S_2Cl_2, both attack tin Sulfur dioxide

[16] *Rec Trav Chim Pays-Bas*, **42** 547 (1923)

reacts with the metal with the formation of stannous sulfide (See also the action of sulfur dioxide and stannous oxide under the latter compound) Dilute sulfuric acid does not readily react on tin in the cold, but the action is accelerated by the presence of oxygen Calvert and Johnson [17] found that when the acid concentration is increased to a concentration corresponding to H_2SO_4 $6H_2O$, the attack is more evident The presence of chlorides in sulfuric acid markedly affects the solution of tin in that acid A mixture of one volume of sulfuric acid, two volumes of nitric acid, and three volumes of water, according to Bassett,[18] dissolves tin in the cold, with the evolution of very nearly pure nitrous oxide and the production of a clear solution of stannic sulfate Tin reacts vigorously with selenium and tellurium when a mixture of the two is heated The reader is referred to the corresponding thermal equilibrium diagrams under tin alloys (p 222)

Tin does not form a compound by direct union with nitrogen It is oxidized by hot nitric acid to hydrated stannic oxide or stannic acids, which see

The soluble salts of tin are few Those which are commercially important are the chlorides, acetates, sulfates, and oxalates All of them show tendencies to hydrolyze Tin in its compounds is amphoteric This phase of its action is discussed in greater detail under the tin compounds

The physiological action of tin has been the subject of widespread study The number of authentic cases wherein tin and its salts have been poisonous is very low, being almost non-existent The stannous salts are believed to be only very slightly toxic, but the stannic salts somewhat more so, according to Vaubel The rarity of tin poisoning, contrasted with the extended use of the metal for cooking vessels and in tin cans for preserving food, shows that the attendant risks are small There are no special pharmaceutical preparations of tin or its compounds, although sometimes tin has been recommended for tapeworm Micheels and de Heen [19] state that a stimulating action on germinating wheat is effected by colloidal tin Gimel [20] found that one part of stannous chloride in 10,000 has a favorable effect on the alcoholic fermentation of yeast

[17] *J Chem Soc*, 19 435 (1866)
[18] *Chem News*, 53 172 (1886)
[19] *Bull Acad Belg*, 1907, 119
[20] *Compt rend*, 147 1324 (1908)

CHAPTER 3

PRODUCTION, DISTRIBUTION, AND CONSUMPTION

Tin is one of the rarest of the base metals and at the same time one of the most indispensable The world's annual production of tin metal is 140,000 to 155,000 tons, of which the United States annually imports and consumes more than 50 per cent This tin metal is valued at over $100,000,000 annually. The production of tin in terms of tons of 2,240 pounds for the years 1920 to 1927 is given in Table 2 These represent primary tin Secondary tin recovered in various forms amounts to approximately 28,000 gross tons per year in the United States American consumers thus take over 105,000 tons of tin annually America's primary tin production is quite negligible

The United States imports no tin ore (except a few tons now and then for experimental purposes), and it has no active tin smelters Several smelters were operated during the World War, but were driven out of the field by English competition, cheaper English labor, and more favorable freight rates

Figure 7 illustrates graphically the sources of tin in the various countries of the world The illustration readily shows that Federated Malay States, Bolivia, and the Dutch East Indies produce approximately three-quarters of the world's supply of tin In the Straits Settlement there are two principal smelters of tin, the Straits Trading Company and the Eastern Smelting Company It is the habit of these smelters to sell daily against their intake of ores, either by disposing of the metal directly or by "hedging" it on the London Metal Exchange Bolivian ores are largely shipped to the Continent, the majority going to England Two of the major producers are the Patiño Mines and Enterprises Consolidated, which is affiliated with the National Lead Company of the United States and the Williams, Harvey smelting company at Bootle near Liverpool, England, and the Guggenheim Brothers who own a number of Bolivian mines and manage others Banka tin is a product of the Dutch East Indies, the name originating from the island of Banka Prior to the World War it sold at bimonthly auctions (about 2,500 tons each auction) in Holland Since the war it has been disposed of by private tender in Batavia, Java Billiton tin

TABLE 2
WORLD'S PRODUCTION OF TIN

World's production of tin expressed in terms of metal obtainable from ore, as reported by Imperial Mineral Resources Bureau through 1925 (with minor changes by American Bureau of Metal Statistics), for 1926-7 substantially as reported by *Mining Journal* In tons of 2,240 pounds

Country	1920	1921	1922	1923	1924	1925	1926	1927	1928
Federated Malay States	34,935	34,491	35,288	37,650	44,042	45,925	45,946	52,176	61,898
Nonfed Malay States	1,992	1,747	1,937	1,727	2,870	2,215	*2,000	*2,000	3,411
Bolivia	27,821	18,804	31,816	29,767	31,610	32,600	29,433	33,858	40,307
Dutch East Indies	21,181	26,382	29,278	29,134	31,558	32,704	33,006	35,298	34,964
China	10,566	11,200	14,000	8,727	7,000	8,880	†6,481	*†4,500	*6,000
Siam	6,201	6,150	6,979	7,684	7,793	6,802	‡9,679	‡10,860	11,218
Nigeria	5,168	5,057	5,123	5,860	6,200	6,506	7,042	7,710	9,044
Australia	5,233	3,592	2,570	3,283	3,069	2,708	*2,700	*2,700	*2,600
Cornwall	3,065	679	370	1,021	1,986	2,339	2,327	*2,400	*2,500
Union of South Africa	1,429	720	470	918	1,162	1,138	§	§	§
Other countries	4,455	4,633	4,355	3,213	3,493	3,675	*3,100	*3,100	*3,000
	122,046	113,455	132,186	128,984	140,783	145,492	141,714	154,602	174,942

* Estimated   † Exports of Chinese tin from Hong Kong to Europe and America were, in 1926, 2,830 tons and in 1927, 1,130 tons   ‡ Includes shipments from Burma, South Africa, and the newly opened fields in Tanganyika and adjoining areas   § Supplies from Union of South Africa probably included with total for Siam

is now largely, if not wholly, smelted in the Straits, and comes out as Straits tin As such it is sold presumably as produced, chiefly to London dealers or hedged on the London Metal Exchange Some ores from Banka are also smelted in the Straits, as well as the ores from Siam, China, Australia, South Africa, Nigeria, and Bolivia Except for some refined tin marketed by China and Australia to the extent of some 10,000 to 15,000 tons per annum, the balance of the output from the last-named countries is shipped in the form of ores or concentrates to English, German, or other smaller Continental smelters Cornish pro-
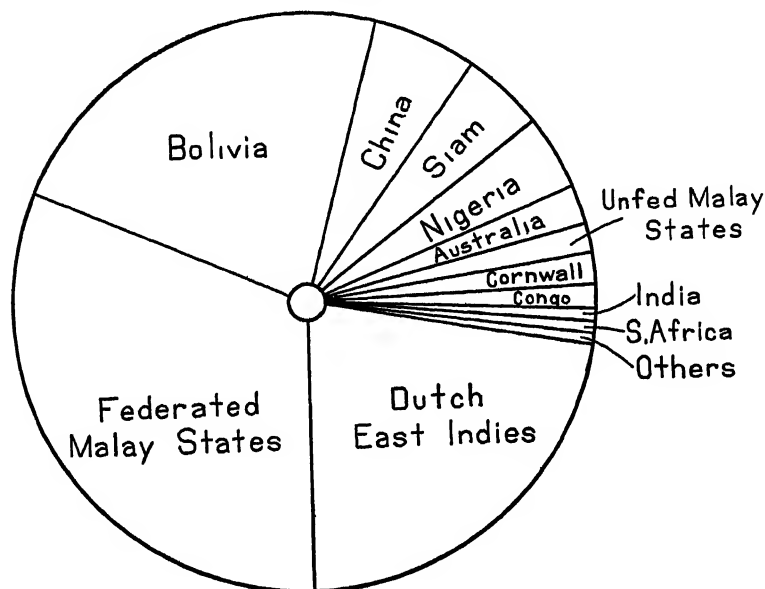

Fig 7 —World's production of tin in 1927, apportioned by countries of origin

duction is, of course, all taken up by British smelters All of the tin, as is the case with Straits, is usually sold concurrently against ore purchases or hedged on the London market Recently, the Penpoll smelting group of the Anglo Oriental Mining Corporation, the London Malayan Tin Trust, Limited, and the Tin Selection Trust, Limited have become an important factor in the tin production of the world Their tin is marketed under the name of Penpoll

Brokers, dealers, merchants, and manufacturers all resort to the same tactics as the smelting companies This hedging practice causes a large volume of business on the London Metal Exchange As a result, there is a large business in options, of which the "put" and the "call"

of tin, the buyers' option to double as well as the sellers' option to double greatly enlarge the turnover and insure a ready market within a reasonable price range, even when transactions are on a large scale, for the disposal of tin on the London Metal Exchange Prices in other countries, both consuming and producing, irrespective of the monetary unit in which they are quoted, are all based on the London price per ton in pounds sterling, converted at the current rate of exchange

Principal Uses of Tin

About 38 per cent of the tin consumed in America goes into the manufacture of tin plate This contains 1 5 to 1 7 per cent of tin America has often been termed the home of the tin can, where it is estimated that we consume and destroy a can per person per day throughout the year in our consumption of canned food products alone The value of tinware produced in the United States annually is more than $260,000,000, the production of some 240 plants

America has more automobiles than any other country in the world We consume an average of 7 5 pounds of tin per car produced

Nearly 90 per cent of the American consumption goes into four main channels tin and terne plate, solder, babbitt, and brasses and bronzes About 35,000 tons are used for tin and terne plate Sixty per cent or more of this tin plate goes into tin cans More than 28,000 tons enter into solder manufacture, an alloy of lead and tin, whose manifold uses are well known More than 22,000 tons are used for babbitt and machinery bearing metals Without proper bearing metals our modern machinery age would be seriously hampered Brass and bronze, particularly ornamental bronzes, high-strength and corrosion-resistant metals, consume 16,750 tons of tin per year Tin oxide (an important constituent of bathtub enamels and similar products, opaque glasses, ceramic glazes), tin chemicals, and other minor uses of the metal consume nearly 15,400 tons of tin per year

Seemingly every year we consume more tin than the total amount imported plus that which is recovered from secondary sources The difference between this figure and the consumption is apparently accounted for by drafts on stocks

Unquestionably, however, a part of this unaccounted-for metal may be attributed to the short service rendered by the finished article and the rapidity with which it finds itself in the melting pot Thus, metal may be re-used several times during the year The accumulated free stocks of tin are never high

Babbitt and bearing metals, brasses and bronzes, castings, white

metal, and type metal are the only uses for tin serving a short period that allow the metal to be re-used, but even these cause considerable losses The metals used in tin and terne plate, solder, foil, collapsible tubes, chemicals, and similar uses are dissipated largely for all time

Tin plate scrap from container manufacturers is the raw material for the detinning companies producing tin chlorides, which is their major product These chlorides are used for the "weighting" of silk
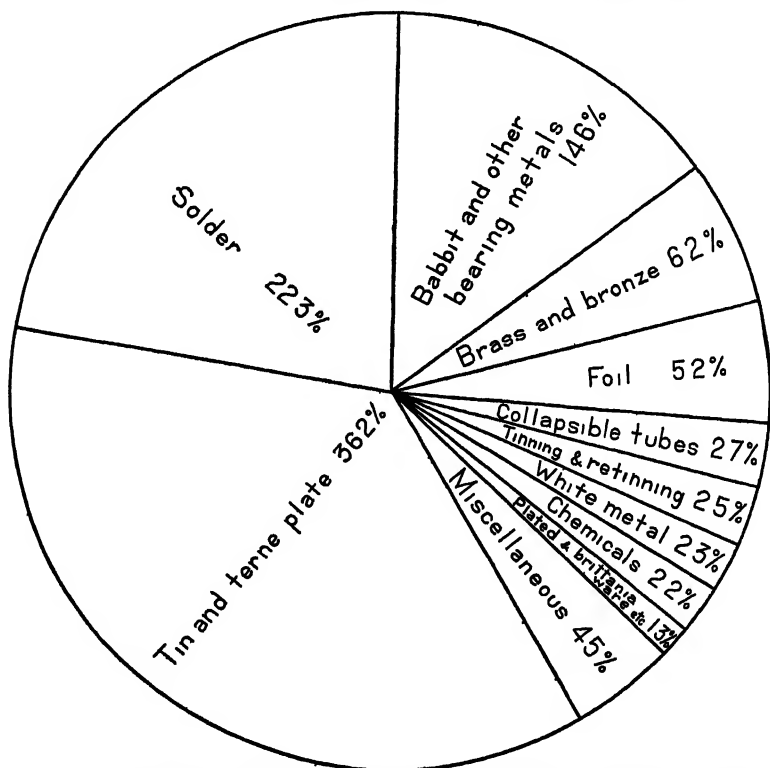

FIG 8—Tin used in principal tin products of American industry in 1917

and in textile printing and dyeing There is considerable recovery of solder from "sweating" old or junked automobile radiators

Census reports state that fire extinguishers and sprinkler systems consume 5,000 tons of tin per year, and refrigerators some 2,500 tons of virgin tin in the form of solder

Aluminum foil in many industries has successfully replaced tin foil for wrapping various products This replacement has caused a decreased consumption of 1,000 tons of pig tin per year in this field

In 1917, as a result of the activities of the War Industries Board, a relatively exact investigation as to where the tin consumed in the United States was finally used resulted in the percentages given in Figure 8 Census figures for the year 1925 show a considerable change in the different places in industry where tin is now consumed The percentage of the total consumption employed in solder has increased but slightly, but the tin plate business of the United States has in-
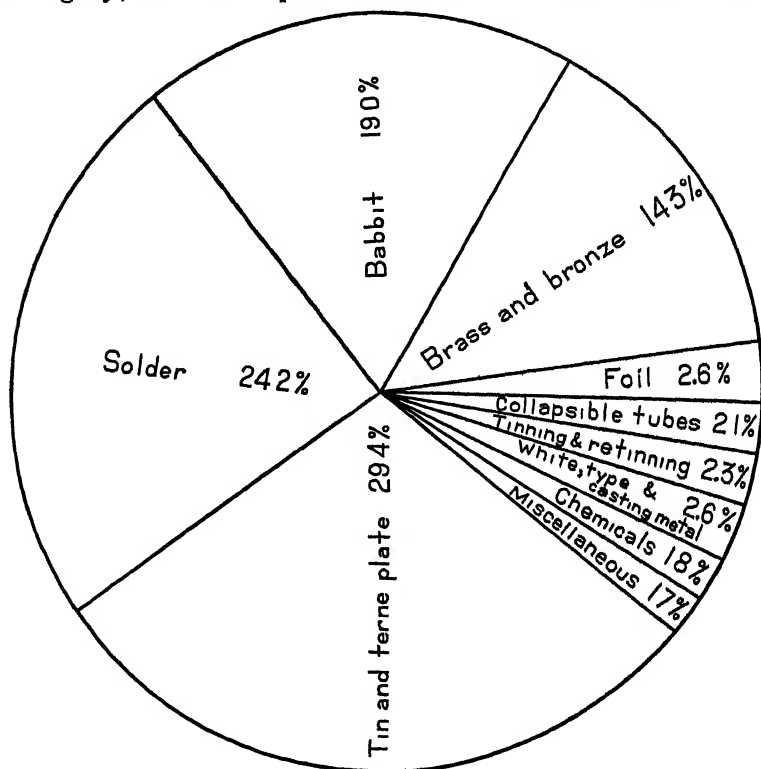

FIG 9 —Tin used in principal tin products of American industry in 1925

creased by leaps and bounds Although at the present time the amount of tin employed per base box of tin plate is smaller, the percentage of the total consumption of tin in the United States used for tin and terne plate in 1928 was 34 2 per cent, in 1927, 33 2 per cent, while in 1925 it was approximately 34 per cent [1] Tin consumed in various other industries for the year 1925 is shown in Figure 9 Since 1917 there has been an appreciable decrease in the percentage of tin used for foil, while babbitt, brass, and bronzes have shown very large increases

[1] *American Bureau of Metal Statistics*

THE PRICE OF TIN

Parsons [2] states that tin is the medium of a vast amount of specu-
lation, particularly on the London Metal Exchange The price of tin
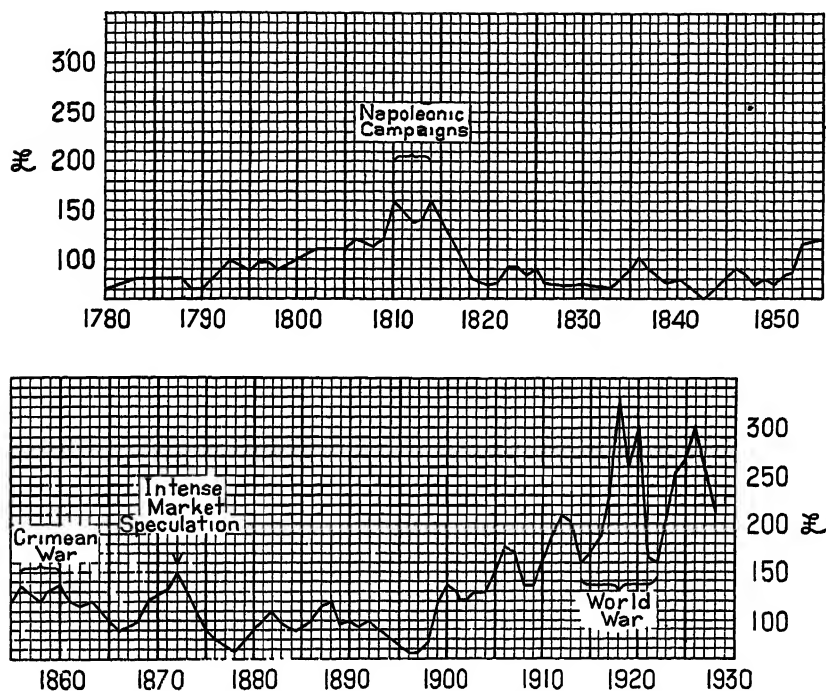for the last 147 years is plotted in Figure 10, in British pounds ster-

FIG 10 —Graph showing average prices of tin metal per ton (2,240 lbs) for the
years 1780-1927

ling per long ton War conditions have markedly affected the price,
causing it to rise rapidly and, at times, in the minds of consumers,
exorbitantly Parsons states

Reports of every kind, from an unusually rainy season in Nigeria to an alleged
depletion of salmon in the waters of British Columbia, are seized upon as bullish
or bearish factors in the tin market The statistics, particularly the figure for
'world's visible supply," are used to an extent out of all proportion to their
month-to-month significance The supply of spot metal being comparatively limited,
it is not difficult to engineer squeezes The big traders alternately take the long
and the short side of the market, reaping profits ultimately from the speculating
public without in any way affecting the actual position of the metal Producers
profess to look with disfavor upon these speculative fluctuations, asserting that
their average realization is less as a consequence of it

² *Eng Mining J* , 125 685 (1928)

It is interesting to note that in the United States during the last twenty years there has been a marked and in some periods a rapid development of what is termed the secondary metal business This is the outgrowth of what was originally a group of operations concerned with the handling of junk, but which now, under increasingly better technical control, is converting our scrap metals into materials of qualities almost equal to that of the virgin materials and constantly endeavoring to reclaim for re-use metals and products which have outlived their usefulness in their original form Figure 11, giving the production of secondary tin in the United States, shows the influence of the secondary metal business on the tin production, or rather, the business of preparing tin metal to add to the available supply, the source of the metal being not ores but old metals The curve shows a steady
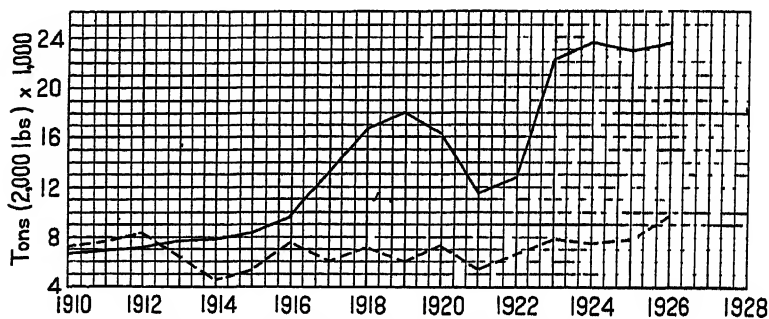

FIG 11 —Secondary Pig Tin in the United States

upward trend with the exception of the period of 1920 to 1922, which is remembered as one of marked industrial depression following the overproduction resulting from the World War The recovery of tin metal both as alloys and as secondary pig tin is receiving greater and more specific attention from American metallurgists and those engaged in the non-ferrous metal business

As a consequence of the secondary metal development, there is always a market now for scrap tin, either as elemental tin metal or in alloys, drosses, ashes, or any other combined form The scrap tin prices for the last five years, as shown in Figure 12, more or less follow the prices of the virgin metal, but of course are lower by the amount or necessary cost incidental to recovery of the tin metal from the form in which it is bought by the secondary metal dealer

One other aspect of the tin situation is a continual emphasis placed upon the fact that the known tin resources of the world are compara-

tively limited The public is constantly being reminded that a tin famine is sure to arrive in the none too distant future This undoubtedly has a sentimental bullish effect on the market However, the officials of the largest tin-consuming companies in the United States have no misgivings as to the future adequacy of the supply either of tin or of any of the other metals Whatever the needs may be, they will be met
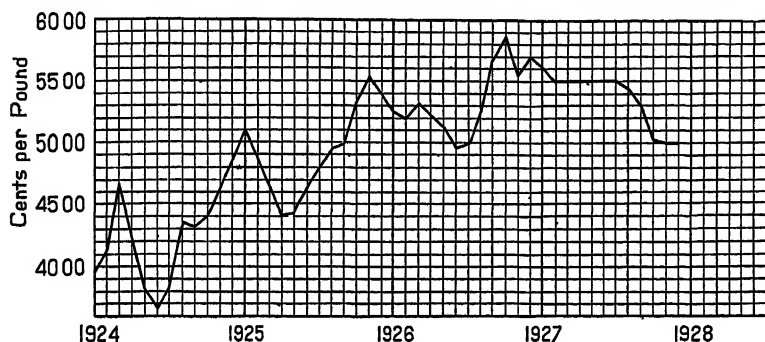

FIG 12 —Scrap tin prices

It is interesting to note that the Amsterdamsche Bank, in its quarterly report to the Government Mining Service of the Dutch East Indies in June, 1927, states that, aside from some unforeseen developments, there is no justification for estimating the world's annual tin output at higher figures than 145,000 to 148,000 tons As to future prospects the report states

If we face the situation in the largest tin-producing countries, the Federated Malay States, there are reasons to believe that no important contribution to an increase of the world's production may be expected from this country In the Dutch East Indies serious efforts have been made to increase the tin production, but the limit will soon be reached there Siam, Nigeria, and Australia still offer a chance for the discovery of new workable alluvial tin fields, which might contribute to an increase in tin exported from those countries Owing to the present political disturbances in China, it seems difficult to give any reliable opinion as to the future production of that country Only Bolivia, where tin is obtained from primary fields, must be able to produce far more than it actually does Finally, although there is but little chance, it is not absolutely excluded that in the near future still some rich tin fields, either primary or alluvial, may be discovered in other countries There are hopes set on "Dark Africa," which continent surprised us in the beginning of this century with its tin fields in Nigeria and Transvaal

However, apart from such surprises, we are not justified in estimating the world's output of tin higher than 145,000 to 148,000 tons Any important influence on tin prices can be caused only by a change in the consumption

Despite the fact that the Amsterdamsche Bank is in an excellent position to judge as to the future, it is exceedingly interesting to note that the world's production of tin for the year 1927 was nearly 10,000

tons greater than what they state would be the maximum figure justi-
fiable Instead of 145,000 tons in 1927, the tin production was greater
than 154,000 tons

Mantell [3] states that the general situation is a difficult one, and many
qualified experts have asserted that any future decrease in price must
come about through a decrease in consumption rather than an increase
in production The more pessimistic believe that the sources for further
supplies are limited and that the present rate of consumption is rapidly
bringing about the exhaustion of the world's tin resources

G T Bridgman, mining engineer for Guggenheim Brothers, New
York, who own large Bolivian mines, foresees a production of tin at
about the present rate for the next ten years, with acute price fluctua-
tions synchronizing with general prosperity, and a "constant, fairly
rapid and virtually complete approach to exhaustion" of the world's tin
resources thereafter, with no limit to the levels to which prices may rise

Even if these predictions were acceptable, it must be pointed out
that they are based upon present knowledge of the technique of mining
and smelting South America and other countries of the world, not yet
fully explored, possess millions of tons of low-grade tin ore which
thus far have no commercial value Sooner or later developments in our
technical knowledge will make them workable and their treatment
commercially necessary and profitable Cornwall, England, whose mines
were thought almost entirely worked out, is now going through a re-
vival stage as a result of high tin prices and the discovery of new
valuable lodes at lower levels through the sinking of deeper shafts
The "free setter" or individual mine owner-operator has again appeared
in Cornwall

In Yunnan, China, the forests surrounding the tin smelters have
disappeared as a result of charcoal manufacture Charcoal is used there
as a smelting fuel They must now change their antiquated methods for
more modern ones The mine owners are only now installing venti-
lating machinery to allow mining at greater depths than formerly
Ore-dressing methods can be greatly improved throughout all of China

The technical branch of tin mining in Bolivia is still backward
Many mines cannot make better than 70 per cent recoveries of the tin
value of their ores, due to inadequate machinery The Bolivian Gov-
ernment is beginning to interest itself in bettering tin-mining practice,
as export duties on tin concentrates bring about three and a third
million dollars to the government Other than the Patiño and Guggen-
heim mines in Bolivia, all mines there need modernization, new equip-

[3] *Iron Age*, 120 545 (1927)

ment, and better ore-dressing machinery to increase metal recoveries The Patiño Mines and Enterprises Consolidated shows net quarterly profits in the neighborhood of three-quarters of a million dollars

Every once in a while we hear reports of intentions or desires to regulate the price of tin It is true that three of the largest operators are in the British Empire The Straits (Malay) Trading Company, producing about 50,000 tons of tin metal annually, Williams, Harvey & Company (Bootle, England), producing about 30,000 tons per year, and the eastern and Cornish smelting companies, contributing something like 25,000 tons annually

There have been rumors lately of steps being taken to bring these three groups together to influence tin prices by artificially creating shortages This attitude would bespeak an entire change of policy for these companies, as they have always been averse to speculation Even, a few years ago, when tin sold at a price which paid very few British-owned mines to operate, efforts to induce mines to close down to influence prices were unavailing

If attempts were made to create a tin shortage artificially, there would be a great impetus toward the development and use of substitutes Experience shows that consumers will adopt almost any kind of expedient to retain their independence We have today the "tinless" can for food products, which year by year will be of greater importance, a tin shortage would bring it into prominence with great speed

Antimony oxide can be and is used to replace part or all of the tin oxide used for enamels Aluminum in the shape of foil has made serious inroads on its tin competitor, perhaps when manufacturing costs are reduced, aluminum collapsible tubes will follow the same trend During the war, cadmium was advocated as a white-metal alloy constituent to replace tin It has possibilities of development which should carry along with it cheaper prices for cadmium as the result of greater production

In Bolivia, it costs $450 to $500 to mine, sort, dress, and concentrate material containing the equivalent of a ton of tin Smelting, usually at a British plant, adds $50 to $60 per ton Export taxes of the various governments, freight, reshipment losses, and smelter's, miner's, and broker's profits make up the remainder of the present price of $1,000 to $1,300 per ton of tin Small mines all over the world cannot afford to operate when tin drops below $850 per ton in the shape of concentrates This artificially keeps up prices, for when the tin price falls below this figure, a large number of small mines close, thus cutting down available supplies until the price again rises, when they reopen

The United States, the largest consumer of tin, seemingly does not face a "hold up" by foreign producers of this important commodity At the present time, it appears that consumption may shortly equal or exceed production, but new technical methods, plant modernization, utilization of lower grade ores, and better mining methods will make available greater supplies of this "semi-precious" metal

In definite contrast to those who believe that the price of tin should rise, Parsons [4] raises the question as to whether 45 cent tin is not a likely possibility for the next few years He states

> The plea is frequently advanced that producers are entitled to higher prices to compensate them for the depletion of their extremely limited reserves, which they imply they are holding as a sort of sacred trust for the benefit of society at large Without imputing to the owners of tin mines any less altruistic ideals than those cherished by owners of other mines, one may venture the opinion that the only motive that would move them to conserve the supply of tin would be the hope of realizing greater profits for themselves in the long run Moreover, they realize full well that a profit of $1 to-day is worth as much as a profit of $2 ten years from now Accordingly, as long as they are earning good profits for their shareholders it is unlikely that directors of tin-mining enterprises generally will adopt a program of curtailment of output The point I am trying to make is that, in spite of the extraordinary speculative character of the London tin market, and the much advertised limitations to the world's aggregate known resources of the metal, the policy of the producers and the broad trend of the market are governed by the same economic laws to which other metals and other commodities are subject

Parsons maintains that the effect of electric dredging in decreasing the price of tin as the result of increased output has been the same as the marked influence of the application of selective flotation in rapidly bringing down the price of lead from nine and a half cents in 1925 to about six cents in 1928 He also discusses the possible applications of substitutes for tin

Parsons also speaks of how low the price of tin can go without squeezing income to the point at which it is deemed more profitable to shut down dredges or curtail production than to produce at normal maximum capacity The earnings of many of the tin companies are not unusual when they reach 50 per cent per annum, and dividends have ranged from 15 to 75 per cent per year In the Dutch East Indies mines, larger and better gravel pumps have been installed In Bolivia, mining and ore-treatment operations have been reorganized In Nigeria, and particularly in Malaya, bigger and better dredges equipped with efficient classifying and jigging machinery have been put into productive operation in recent years, some displacing older and less efficient dredges and others starting operations on deposits where dredges have never been used Parsons sees the decline of tin prices as a natural con-

[4] *Eng Mining J ,* 125 685 (1928)

sequence exactly analogous to the well-known and often-told story of the progress in the mining, milling, smelting, and producing of the other non-ferrous metals

The marginal producers whose costs are above the average have been mentioned previously Consideration must be given to the operations of the Chinese who, according to the best estimates, contribute about 45 per cent of the Malayan production by so-called hand mining This situation is best discussed in Parsons' own words

It is argued in some quarters that lower prices will cause a decided shrinkage in output from this source On the other hand, consider the following view of the situation The miners are there on the ground, their position is like that of a farmer with a single "money" crop They are not particularly concerned with conserving the world's supply of tin nor with the depleting of their own ore reserve They are sure of a market at some price for all the concentrate they can produce, if they work harder than they have been working they can produce more tin, thereby offsetting the effects of lower prices and still maintain their income Perhaps the cost of production is high, but labor is the one big item in the cost, and if no other means of earning a living is at hand, the average Chinese is likely to dig tin for whatever he can get Incidentally, there has been a trend toward the purchase of large modern gravel pumps among the Chinese, so that it is probable that many of them can produce more cheaply than ever before To conclude that a decline in the price, say to forty cents, would seriously affect Chinese production appears to be unwarranted

In 1928 it is interesting to note an editorial discussion in the August 16 issue of *The Iron Age* from which the following quotation is taken

Marketwise tin is by far the most mysterious of the familiar metals It is notable that those most fully posted frankly state that virtually they know almost nothing It is impossible to measure closely the influence of price upon production but the influence upon consumption is a more open matter

The changes (in tin consumption) represent accomplishments and there is no reason for assuming that cheap tin would result in a reversion to older practices There might, however, be expansion of tin consumption in new uses So much has been done that little room seems to be left for further economies, and the industries using tin promise continued expansion In the last 15 years, United States consumption has increased considerably more than that of the rest of the world and thus there are chances of consumptive demands elsewhere having a large increase

Propaganda of long ago that tin production could not be greatly increased is exploded, for it has increased and there has been much progress in the technique The working of alluvial deposits has been extended to leaner gravels, for with the improved dredging equipment and the use of gravel pumps, facilitated by operations passing into strong hands with command of capital, a half pound of tin per cubic yard is workable against one and a half pounds formerly

Both supplies and consumption of tin have increased this year World supplies in the first half of the year were reported at 62,249 gross tons, or 4,034 tons increase over the first half of last year Deliveries are reported at 61,751 tons, or 2,848 tons increase The visible supply increased 498 tons, against a decrease of 688 tons in the first half of last year In the Federated Malay States production has increased, and last year, stimulated by the high prices of 1926 and 1927, it was 52,176 tons or 13 5 per cent more than in 1926 This year (1928) it has been running 20 per cent higher than in 1927, but with the lower prices of recent months the higher cost workings may do less

J H Lang[5] states that there is a consistent refusal to have any tin marketed at home (in the United States), and that there is an insistence on conferring all the benefits and advantages accruing from the tin trade upon England He further states

London stands between the producer and consumer, furnishing to both the only real market that exists in the world, using in the process that keen trading instinct and fine appreciation of values and the capacity and courage which come from long experience In some quarters the simple-minded idea is entertained that, by going direct to the source of supply and ignoring the London market, the activities of the latter and its influence on prices will be curtailed The ostrich has made himself ridiculous by adopting similar tactics Some day the trade may be educated to a point where it will realize the advantages of keeping its business at home, and using it to stimulate and develop a real market in this country, with all its machinery and its power and influence under our own control

All things considered, tin is sold cheaper in America than anywhere else Nowhere else is competition so keen and nowhere else are the margins of profit (when they exist at all) so narrow Anyone who does not believe this has only to go to France, England, Germany, Italy, or any other country, to have the statement confirmed Offers are cabled from London daily to agents and representatives on this side of the water to be sold on a purely commission basis Minimum wholesale lots are five-ton quantities Pigs of tin weigh close to 100 pounds each There is no legitimate importing or merchandising profit in the business New York has no separate entity of its own in the tin market, but slavishly follows prices made in London It is a bad case of the tail wagging the dog Those who wish to deal in the metal, consumers or others who wish to sell, or "hedge," or in any way switch their deliveries or commitments, are compelled to meet this competition, with the result, as above stated, that by and large and over a period of time New York is the cheapest market in the world

QUALITIES OF COMMERCIAL TIN

The New York Metal Exchange had recently been reorganized and was making a definite effort to establish a tin exchange in America Two important classes of tin were bought and sold in the United States These are commonly known, according to the specifications of both the London and the New York Metal Exchanges, as standard or Straits tin, and 99 per cent tin On contracts calling for standard tin, Straits, Australian, Banka, Billiton, American Electrolytic when it existed, and English Refined tin were deliverable at contract prices Other virgin refined tins also fell into this class, provided they assayed not less than 99 75 per cent tin On contracts calling for 99 per cent tin, any brand of tin assaying not less than 99 per cent of the metal and approved by the Exchange was good delivery

On December 1st, 1928, the New York Metal Exchange ceased to exist, and its activities were absorbed by the National Metal Exchange It follows practices which have proved successful in London The specifications and types of tin in which it deals are the same as those on the London Metal Exchange Twenty-four brands of tin are traded

[5] "Marketing of Metals and Minerals," McGraw Hill Book Company, Inc, New York, 1925.

against its contracts Class *A,* deliverable at contract price, includes Banka, Straits (Straits Trading Co, Eastern Smelting Co, Po Hin, Ban Hok Hin), English Refined (Williams Harvey Mellanear refined, Penpoll Special refined, Cornish refined, Capper Pass & Son), German Refined (Th Goldschmidt "Baum," Berzelius "Rose Brand," Zinn-werke Wilhelmsburg refined), Belgian Refined (Union Miniere du Haut Katanga), Australian Refined (O T Lemprieie & Co, Mt Bischoff, Pyrmont) Class *B,* delivered at 1⅛ cents per pound under contract, consists of English Common (Williams Harvey Mellanear common, Penpoll common, Cornish common, Thames Metal Co), German Common (Th Goldschmidt "Volta," Th Goldschmidt "Tego," Zinnwerke Wilhelmsburg common), and Chinese Tin No 1 Although the National Metal Exchange may in time broaden its field of activity, it at present confines its dealings to Standard tin futures, with no pro-vision for trading in Straits or any other specific qualities of tin As a result of this restriction, the American Tin Trade Association has been formed to handle Straits or specific qualities of tin, acting as a complementary organization rather than a competitor of the National Metal Exchange

Tins are sold by brands which are either indicative of the origin of the ore from which the tin was smelted or else are indicative of the smelter, carrying his name or trade mark The tins from alluvial ores, when made by straight pyrometallurgical methods, are purer, while those from vein ores are generally poorer Table 3 gives tin analyses of a large number of brands on the market

The selling and buying of tin metal are regulated by contracts of the various exchanges These contracts are very specific as to general conditions, deliveries, and methods of making shipment Ordinarily no delivery of less than five tons is valid All of the conditions entering into the bartering of tin metal are given in the following specific-quality tin contract of the American Tin Trade Association, Inc

TABLE 3
TYPICAL TIN ANALYSIS *

	Tin	Antimony	Arsenic	Lead	Bismuth	Copper	Iron	Silver	Sulfur	Cobalt
American Electrolytic tin	99 928	0 002	0 002	nl	0 042	0 026	trace	nl	trace	
Banka	99 950	0 007	nl	trace	nl	0 018	0 045	nl	nl	
Billiton	99 960	0 006	nl	nl	nl	0 023	nl	nl		
Penang	99 939	trace	0 013	trace	nl	0 016	0 028		0 004	
Singapore	99 870	0 008	0 045	0 034	0 003	0 052	0 003		0 004	
Mt Bischoff	99 847	0 015	0 015	0 042	0 001	0 017	0 063	0 006	0 005	
Pyrmont	99 795	0 015	0 063	0 037	0 005	0 035	0 042	trace	0 008	
Irvine Bank	99 938	0 017	0 019	trace	nl	0 022	trace	nl	0 004	
Mellanear, Lamb & Flag	99 580	0 062	0 034	0 221	0 025	0 126	0 002	0 018	0 004	
Williams, Harvey & Co	99 190	0 160	0 060	0 160	0 350	0 060	0 020			
No 1	99 860	0 015	0 040	0 004	0 005	0 047	0 003	nl	0 006	
No 2	99 560	0 166	0 037	0 162	0 007	0 050	0 005	trace	0 013	
No 2-a	99 350	0 245	0 065	0 223	0 015	0 042	0 016	trace	0 013	
No 3	99 200	0 300	0 037	0 396	0 007	0 100	0 013	0 014	0 006	
No 4	99 941	0 011	0 022	trace	0 001	0 020	trace	trace	0 005	
Redruth	99 160	0 176	0 053	0 177	0 017	0 445	0 041	0 006	0 008	
O T Lempriere & Co	99 880	0 011	0 016	0 019	0 012	0 026	0 020	nl	trace	0 012
Cornish Refined	99 880	0 012	0 006	0 014	trace	0 046	0 003		0 017	0 008
Cornish Lamb & Flag	99 321	0 174	0 034	0 068	trace	0 205	0 040		0 044	
German Lamb & Flag	99 080	0 150	0 080	0 500	0 060	0 080	0 050			
Th Goldschmidt										
No 1	99 860	0 004	nl	0 102	nl	0 043	trace	nl	trace	
No 2	99 460	0 015	nl	0 425	nl	0 069	trace	nl	trace	
No 3	99 150	0 122	0 046	0 143	0 112	0 352	0 007	0 006	trace	
Sutton, T & Sons	99 550	trace	0 022	0 342	0 015	0 045	0 010	trace	nl	trace
Chinese No 1	99 343	0 031	0 040	0 434	0 007	0 052	0 010	trace	0 011	0 072
Wing, Hong & Co										
No 2	98 662	0 039	0 035	1 035	0 012	0 134	0 014	trace	0 011	0 058
No 3	95 280	0 381	0 050	3 995	0 020	0 106	0 026	0 018	0 008	0 116

TABLE 3—*Continued*

	Tin	Antimony	Arsenic	Lead	Bismuth	Copper	Iron	Silver	Sulfur	Cobalt
Penpoll										
No 1	99 720	0 118	0 054	0 041	0 007	0 052	0 004	0 009	0 007	
No 2	98 710	0 569	0 042	0 546	0 055	0 103	0 007	0 015	0 004	
No 3	99 300	0 325	0 056	0 212	0 050	0 088	0 002	0 021	0 009	
Special Refined	99 9309	0 019	trace	0 0256	0 0015	0 0102	0 0087	trace		
Refined	99 800	0 118	0 054	0 041	0 007	0 052	0 004	0 009	0 007	0 0041
Capper Pass Chempur	99 9946	trace	trace	trace	trace	0 0038	0 0016			Zn trace

* This table is a composite one, values being taken from Jones, "Tinfields of the World," Liddell, "Handbook of Non Ferrous Metallurgy," "Metal Statistics 1928," and private communication from W A Cowan of the National Lead Co

SPECIFIC QUALITY TIN CONTRACT

Printed and Issued by

AMERICAN TIN TRADE ASSOCIATION, INC

As adopted, effective on and after December 1, 1928

NEW YORK,

AGREE TO SELL

AND   AGREE TO BUY

QUANTITY

DESCRIPTION

PRICE

DELIVERY

SHIPMENT

PAYMENT

OTHER CONDITIONS

The following rules are a part of and shall govern this contract subject only to such modifications thereof as may be agreed upon by the parties in writing

RULE 1—General Conditions

(A) Where tons are mentioned in this contract, gross tons of 2,240 pounds shall be understood unless otherwise specified

(B) Unless otherwise specified, tin shall be weighed in lots of 5 tons each by any weighmaster appearing on the official list of the Association Each lot of 5 tons shall be of the same brand and in one warehouse or at one dock in the Port of New York

(C) On contracts for 25 tons or more, deliveries must be made in lots of 25 tons or more at one time and in one place, unless otherwise specified or agreed upon between buyer and seller

(D) On contracts for less than 25 tons, unless otherwise specified or agreed upon, delivery must be made at one time and in one place

(E) Unless otherwise specifically agreed in writing, the obligations of contracting parties shall not be altered or impaired by instructions issued or accepted by either party to deliver, ship or receive tin under this contract

(F) All contracts for dealings in tin shall be written by seller, except where a broker has been employed, in which case they shall be written by the broker, and accepted respectively by the buyer and seller Such acceptances shall be made promptly in writing

(G) Any imposition or change of duty or tax on sales, consumption, turnover, or any other tax levied or imposed by the Federal or State Government shall be for buyer's account unless otherwise specified by law

(H) In the event of either party to a contract failing either to deliver or to accept and pay for the tin properly tendered under a contract, the party who shall suffer by such default may either sell or purchase an equivalent amount either on the day of said default or upon the next following business day, either in the open market or at private sale, and any difference arising from such action shall be charged by him to the said party in default who shall promptly pay the amount thereof to the party to whom he is in default

(I) If before the maturity of any contract either party thereto shall suspend payment, or be a defaulter, or commit an act of bankruptcy, or issue a notice convening a meeting of his creditors, or become bankrupt or insolvent or become unable to meet his general trade obligations in the regular course of business, or shall fail to deposit margins as herein after provided for, that contract shall thereupon be closed out immediately, and all differences between the contract price and the price at which the tin may have been sold or bought, as the case may be, shall constitute the rule and measure of damages

(J) Deliveries shall be made by the first issuer of delivery order, and/or the first tenderer of warehouse receipt, not later than noon on all business days except Saturday, when such deliveries shall be made on or before 10 A M Re deliveries shall be made by intermediate parties without delay until 11 45 A M on Saturdays or 2 45 P M on all other business days.

(K) Holders of storage receipts shall be responsible for accrued storage

(L) Buyer shall have until 5 P M of the day following delivery (Sundays and legal holi days excluded) in which to remove the tin from docks or warehouses, after which all expenses to be for buyer's account

(M) When one party has a contract with another, corresponding in all respects, except as to price, with another contract between said parties, settlement of such contracts shall be made by a cash payment of the amount arising as determined by the difference in price named in said contracts, the time of such payment to be on the earliest date of delivery permissible under the contract In the event of vessel having been declared on such con tracts, settlement shall be due and payable on the day following the date of arrival of said vessel, but where no vessel's name has been declared difference shall be settled within 60 days after the earliest date of shipment under the contract, except where ship ment is to be made from United Kingdom or Europe, when settlement shall be made not later than 14 days after the latest date of shipment under the contract

(N) An excess or deficiency of more than one (1) per cent in the weight of each parcel of five tons shall not be a good delivery

(O) If seller, by reason of strikes, accidents, delays or other contingencies beyond his con trol, is prevented from making delivery or shipment as called for by contract, he shall immediately notify the buyer thereof, who may then appeal against such postponement to the Board of Directors who, after hearing both parties to the contract, shall decide upon the merits of the question at issue by a denial of the postponement or by granting of such reasonable extension of time as seems warranted by the circumstances

(P) Payments, unless otherwise specified, shall be made in New York funds immediately upon presentation of invoice, weight certificates and delivery order and/or warehouse certifi cate and/or bill of lading

(Q) Either party to a contract may call the other party thereto to deposit with a Bank or Trust Co in the Borough of Manhattan, City of New York (which shall be a member of the New York Clearing House Association and/or the Federal Reserve System) a margin sufficient to cover the depreciation or appreciation from the said contract price to the market value of the tin on the day of the call The party so called will imme diately deposit in the Bank or Trust Company selected by him the amount necessary to cover such depreciation or appreciation in the said contract price, taking as evidence of such deposit from the Bank or Trust Company their original and duplicate certifi cate of deposit, which shall be in the usual form, and made payable "to the party so depositing and/or to the other party to the contract, as the Secretary of the American Tin Trade Association Inc, shall direct" The depositor shall immediately deliver to the Secretary of the American Tin Trade Association, Inc, the original "Certificate of Deposit," who shall hold the same until such time as both parties to the contract shall notify him that the margin may be released

RULE 2—Deliveries Ex Dock or Warehouse

(A) Deliveries from warehouses in the Port of New York shall be made only from ware houses named in the official list of the Association

(B) When tin is sold for delivery ex dock or warehouse Port of New York and the day of delivery is not specified, first seller shall furnish first buyer with notice of delivery, in writing, or by full rate telegram filed, not later than 12 o'clock noon (or not later than 10 A M on Saturdays) on the day which precedes by two business days the day of delivery Re declarations under such notice shall be made without delay until 2 30 P M (or until 12 o'clock noon on Saturdays) When said notice specifies a steamer and the tin is not available on the day stipulated, it shall be delivered as soon thereafter as it is available without further notice

(C) When tin is sold for delivery from a named vessel afloat or a named vessel at dock, the notice provided for in Section "B" of this Rule is not required, but seller shall make delivery promptly when the tin is available for delivery and seller shall make all reason able efforts to expedite delivery

(D) When tin is sold for spot delivery, such delivery must be tendered on the business day next following the date of sale

(E) The tender of negotiable warehouse receipt properly endorsed for tin in warehouse, or delivery order for tin on dock, in either case accompanied by weight certificates, shall constitute a good delivery

(F) Unless prior notice has been given of earlier delivery as provided in Rule 2, Section "B," tin sold for delivery ex dock or warehouse Port of New York during a given month shall be delivered on the business day next preceding the last business day of the month, and this rule is to apply also when tin is sold for delivery during the second half of any given month, and tin sold for delivery during the first half of any given month shall be delivered not later than the business day next preceding the 15th day of said month

RULE 3—Import Shipments

(A) Shipment may be made by steamers and/or motor ships at seller's option

(B) Shipment shall be made direct to port of discharge, except from the Far East, where the seller shall have the option to make shipment via United Kingdom or European ports for trans shipment thence by first available steamer and/or motor ship, providing original Far East bill of lading shall carry the optional clause for trans shipment therefrom

(C) The term "prompt shipment" shall be considered to be within a period of 14 days from United Kingdom or Europe, and within 30 days from the Far East

(D) The date of signed copy of bill of lading shall determine the date of shipment on all tenders made from vessels sailing from port or ports named in this contract

(E) The date of vessel's entry at Custom House shall fix the date of arrival at port of dis charge

(F) Declaration of shipment shall, at the request of the buyer, be made by seller in writing, and/or by telegram, cable or radio, within 10 days of the date of shipment from United Kingdom, or Europe, and within 30 days of the date of shipment from the Far East, except as hereinafter provided for

(G) On contracts for shipment from the Far East entered into 30 days or more after the date of shipment, the seller is privileged to make declaration within 3 days, though it over laps the time stipulated in Section "F" of this rule

(H) No declaration of shipment under Sections "F" and "G" of this rule shall be valid unless made prior to arrival of the declared vessel at port of discharge, nor shall a declaration be valid if a known accident, imperiling the arrival of said vessel within the usual period of her transit time between port of loading and discharge, shall have happened prior to the date of such declaration

(I) Where a vessel's name has been declared and the vessel is lost the contract is void, but in case of only partial loss the contract is to hold good for such portion of the metal as may come forward for the seller's account, providing such portion be not claimed by the underwriters

(J) Seller having made declaration under this contract may not change same except with buyer's consent However, if accidents or other causes, beyond seller's control, prevent the arrival of tin by vessel or vessels originally declared, and the tin arrives by another vessel or vessels, delivery shall be valid upon the arrival of the tin

(K) On c i f contracts seller shall not be obligated to furnish insurance in excess of the con tract price

(L) No bill of lading to be for more than 25 tons

(M) Shipping documents to consist of (a) Consular invoice (or a written guarantee to furnish same within six months, (b) full set of bills of lading, (c) policy or underwriter's certifi cate of insurance (loss, if any, payable in either New York or London) In the event of any of the two last named of these documents being missing, bank guarantee shall be given for the production of same on buyer's request

RULE 4—Domestic Shipments

(A) Prompt domestic shipment shall be made within seven days, exclusive of holidays and Sundays.

(B) When tin is sold for domestic shipment or delivery f o b New York, shipment or delivery, unless otherwise agreed upon, may be made at seller's option at any time during the period specified in the contract

(C) On contracts for carload lots or more for domestic shipment f o b New York, it shall be considered proper fulfillment by the seller if he presents delivery order for tin on dock or in warehouse in the Port of New York to railway or transportation company not later than 4 30 P M on the business day preceding the last business day of the period covered in the contract

(D) Buyer must furnish shipping and/or delivery instructions within 3 days on written or telegraphic request providing such request is made by the seller 3 days before or during the stipulated period for shipment f o b New York

(E) When tin of a carload quantity is sold for domestic shipment or delivery f o b New York it is understood that seller is obligated to make shipment or delivery at one time and to only one place or destination and by one routing unless otherwise agreed upon

(F) The stipulations contained in Section "J" of Rule 1, and Section "B" of Rule 2, shall not apply when tin is sold f o b car or steamer New York

RULE 5—Disputes and Arbitrations

(A) Any claim, dispute, difference or controversy between the parties hereto arising out of or under this contract shall be settled by arbitration, as follows Either party may, by writ ten notice to the other, appoint an Arbitrator Thereupon, within five days after the giving of such notice, the other shall, by written notice to the former, appoint another Arbitrator, and in default of such second appointment the person who is at the time acting as President of the American Tin Trade Association, Inc, shall appoint the other Arbitrator upon a written request from either party to the dispute When any two Arbi trators have been appointed as aforesaid, they shall, if possible, agree upon a third Arbi trator and shall appoint him by notice in writing, signed by both of them in triplicate, one of which triplicate notices shall be given to each party hereto, but if five days shall elapse after the appointment of the second Arbitrator without notice of appointment of the third Arbitrator being given as aforesaid, then at the written request of either party hereto (or both) the person who is at the time acting as President of the American Tin Trade Association, Inc, shall appoint the third Arbitrator All Arbitrators appointed hereunder must be members of the American Tin Trade Association, Inc Upon appoint ment of the third Arbitrator, as hereinbefore provided (whichever way appointed as aforesaid) the three Arbitrators shall meet and shall give opportunity to each party hereto to present his case and witnesses, if any, in the presence of the other, and shall then make their award, and the award of the majority of the Arbitrators shall be binding upon the parties hereto and judgment may be entered thereon in any court having jurisdiction subject only to appeal as hereinafter provided for Such award shall include the fixing of the expense of the arbitration and assessment of same against either or both parties.

(B) Liberality of procedure is to be observed and such methods are to be followed by the Arbitrators as will be best calculated to elicit all the evidence pertaining to the case The Arbitrators shall conduct the arbitration with the end in view of establishing and enforc ing equity and fair dealing in matters of trade and commerce, irrespective of technicali ties, and with the least possible delays and expenditures consistent with a comprehensive

investigation of each controversy presented The spirit of conciliation should guide the Arbitrators in their conduct of the proceedings, and they should endeavor to remove all doubts and misunderstandings between the parties so as to effect, if possible, a harmonious disposition of the controversy

(C) The following regulations shall govern all arbitrations held under this contract Five written copies of all complaints specifically alleging the particular act or acts complained of, shall be delivered to the Secretary of the Association accompanied by all the documentary evidence bearing upon the case in the possession of the complainant or complainants, and by a list of the witnesses by whom it is proposed to prove the allegations of the complaint Both parties shall be duly notified of the date of hearing, which shall be held not later than ten business days from the receipt of original complaint, and shall be entitled to be present thereat

(D) Award—The award of the Arbitrators shall be final and binding on both parties (unless within five business days after receipt of the award, written appeal therefrom together with a fee of $50 00 be lodged with the Secretary of the Association by either disputant) Settlements under an award of the Arbitrators shall be made within ten days from the date of such award in cash

(E) Appeal—In the event of an appeal from a decision of the Arbitrators such appeal shall be presented in writing by the appellant to the Board of Appeals, who shall thereafter give at least five days' notice, exclusive of legal holidays, to the interested parties of the time and place where they shall consider the case The appellant and respondent shall deliver to the Secretary of the Association seven copies of a brief or statement covering the case Such brief or statement duly sworn to shall be delivered to the Secretary of the American Tin Trade Association, Inc , at least 48 hours before the time set for the appeal Not less than five members of the Board of Appeals being present, the decision of said Board or the majority thereof shall be the final and binding decision If, on any appeal any member of the Board shall be an interested party in the contract his place shall be taken for that appeal by an Alternate

(F) Fees—The fees for arbitration shall be $25 00 in each case, and if an appeal is made there shall be an appeal fee of $50 00 payable to the Association Unless otherwise divided or awarded by the Arbitrators or the Board of Appeals, the fees for arbitration or appeal shall be finally paid by the losing party In event of arbitration between a member and non member of the Association the member must guarantee the payment of the fees or the non member must deposit the fees with the Secretary before the arbitration is held, and adjustment shall be made after the award has been rendered

(G) Oaths—In all arbitrations and appeals the Arbitrators, and/or members of the Board of Appeals shall before acting, subscribe to the usual legal oath of office In all arbitration and appeal hearings all witnesses and the principals giving oral evidence shall be duly sworn in the usual manner Awards must be legally acknowledged

Accepted

CHAPTER 4

ORES AND ORE DEPOSITS

CHARACTERISTICS OF TIN ORES

Cassiterite, or tinstone, is the only mineral that is an important source of tin This mineral is frequently called "tin ore " The use of the term should be restricted to the ore containing the mineral, and not, in addition, to the concentrates of the mineral obtained from the ore or from stanniferous alluvial deposits There is a general misuse of the term tin ore in the Malay Peninsula and adjacent localities, particularly where most of the mineral is obtained from secondary stanniferous deposits The term cassiterite is exclusively used in mineralogical, geological, and other scientific writings It is unfortunate that it is not more frequently used when referring to the occurrence of the mineral on an economic scale

Tinstone is a very convenient old English term deserving a more frequent use Tinstone is a dioxide of tin, or stannic oxide When chemically pure, as in the very rare transparent variety, it has a metallic content of 78 6 per cent tin Frequently, however, the crystals and grains contain appreciable amounts of impurities, chiefly iron and tantalum The impurities here referred to are those actually in the mineral itself We are for the present unconcerned with the usual impurities found in tinstone concentrates Ainalite is a variety of cassiterite containing almost 9 per cent of tantalum pentoxide Tinstone usually has a deep brown or black color with an adamantine luster Several other colored varieties are known, among them being red ruby tin, yellow rosin tin, and yellow wax tin, the names in each case being descriptive of the mineral's appearance Sparable tin, tooth tin, and needle tin, as a result of their acute ditetragonal pyramidal crystalline form, receive their names from their crystallographic appearance Wood tin is a compact variety of cassiterite composed of radiating fibers resembling dry wood Toad's eye tin is a similar variety on a smaller scale in which the fibers appear to resemble the eye of a toad Stream tin is water-worn tinstone Float tin is sometimes employed to describe the cassiterite occurring in soil derived from the weathered surface of a mineralized area

The crystals of cassiterite belong to the tetragonal system Common forms are tetragonal prisms terminated by tetragonal pyramids Figure 13 shows the structure of well-formed crystals Twin crystals are common, one modification known as the kneecap twin being more prevalent Well-defined crystalline forms readily recognizable are more frequently absent than present Cassiterite also occurs massive and as grains, often in reniform shapes with radiating fibrous structure such as wood tin It is brittle and has a subconchoidal fracture The broken surfaces are frequently uneven with a resinous appearance Cassiterite is about as hard as ordinary steel, having a value of 6 to 7 on the Von
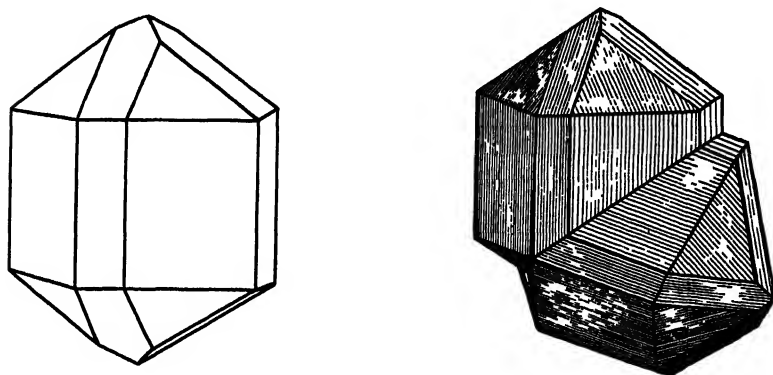
Fig 13 —Crystals of cassiterite

Moh mineralogical scale Its specific gravity varies in different varieties from 6 4 to 7 1, which is unusually high for a mineral with a non-metallic luster The high specific gravity of tinstone is one of its fortunate characteristics It is about two and one-half times as heavy as quartz sand (specific gravity 2 65), two and one-third times as heavy as tourmaline (specific gravity 3), and about one and one-third times as heavy as ilmenite (specific gravity 4 5 to 5), magnetite (specific gravity 4 9 to 5 2), and hematite (specific gravity 4 5 to 5 3) It is frequently associated with these minerals Its higher specific gravity makes it readily separable by panning, by the use of sluice boxes and shaking tables

Cassiterite is ordinarily considered to be infusible When the finely powdered mineral is treated with the blowpipe on charcoal with a mixture of sodium carbonate and charcoal powder, it gives a globule of tin with a coating of white tin oxide Fusion mixtures of cyanides readily reduce tinstone to the metal If the mass resulting from the fusion of the mineral with sodium carbonate be moistened with cobalt

nitrate and again strongly heated, a characteristic blue-green color is produced It is practically insoluble in almost all chemical solutions or mixtures of such solutions, a characteristic which is not shared by stannic oxide artificially prepared in the chemical way

Stannite is an ore of tin of lesser importance than cassiterite It is a sulfide of tin, copper, and iron, sometimes known as tin pyrites or bell-metal ore Its chemical composition is sometimes expressed by the formula Cu_2S FeS SnS_2 with zinc usually present in varying quantities The tin content varies from 22 to 27 per cent with about 29 per cent of copper, 13 per cent of iron, and 30 per cent of sulfur Crystals are rare, but when they do occur are found to be of the cubic system The color of the mineral is steel gray when pure, but the usual variety is frequently iron black, sometimes bronze or bell-metal color, and occasionally with a bluish tarnish The presence of an admixture of copper pyrites causes the mineral to assume a yellowish color Stannite has a metallic luster and gives a blackish streak Its specific gravity is 4 3 to 4 5—being considerably less than cassiterite—with a hardness of 4 on the Von Moh scale When heated in an open tube it gives off sulfur When treated by the blowpipe on charcoal, it eventually fuses to form a brittle metallic globule The reactions for iron and copper are given by the roasted mineral with borax It is only in Bolivia that stannite has been proved to occur in quantities of economic importance In some of the old Cornish mines its appearance and working are only sporadic Stannite is an unstable mineral It is thought that probably most of the tin oxide known as wood tin is of secondary origin after stannite

A few grains of native metallic tin have been reported to occur in one or two tin fields Investigations of such occurrences have generally shown them to be nothing more than ancient smelted products, such as the Jew's house tin occasionally found in Cornwall Irregular rounded grains of native tin have been reported from some of the gravels of the Aberfoil and Sam Rivers of New South Wales It is very probable, however, that this so-called native tin was a thin film of the metal on the surface of tinstone grains due to the natural reduction in the presence of dilute sulfuric acid from decomposing pyrite and a metal This reaction will be discussed a little later under the field test for tinstone It may be almost positively stated that tin does not occur native

Cylindrite has in recent years been discovered in Bolivia in sufficient amount to justify special ore-dressing methods for milling it It owes its name to the cylindrical shell-like fragments into which it cleaves It is a complex lead-tin-antimony sulfide, its composition being repre-

sented by the formula $Pb_6Sb_2Sn_6S_{11}$ Its color is blackish lead gray, its luster metallic, its streak black Its specific gravity is much lower than cassiterite but higher than that of stannite, being 5 42, but it is much softer than either of the other minerals, being 2 5 to 3 on the Von Moh scale It is often associated with stannite and cassiterite in veins along with franckeite, sphalerite, pyrite, proustite, and quartz A typical high-grade specimen of cylindrite is a compact lead-gray mixture of sulfides which are quite soft and dirty the hands The cylindrical shells of cylindrite are prominent on the broken surface of the ore

Another complex sulfide of tin is franckeite, which is very similar to cylindrite except that it has perfect cleavage in one direction It is a blackish-gray to black mineral with a metallic luster It is generally associated with cylindrite Its composition is represented by the formula $Pb_5Sb_2Sn_2S_{11}$, containing therefore a smaller percentage of tin than cylindrite Its specific gravity is slightly higher than cylindrite, being 5 5, and its hardness is approximately the same as the latter mineral, being 2 75 on the Von ·Moh scale Franckeite often occurs massive with imperfect radiated and foliated structure It is found in certain veins in Bolivia associated with the same minerals ordinarily found along with cylindrite

There are a number of other sulfide minerals containing tin, most of which, however, are rare For completeness they are mentioned here canfieldite, teallite and plumbostannite The borates nordenskioldite, hulsite, and paigeite also contain tin Stokesite is a tin silicate which exists only as rare specimens of no commercial importance although of considerable scientific interest Certain tourmaline hornfels rocks from Ear Mountain in Alaska contain a coal-black mineral which seems to resemble the associated granular tourmaline This material, however, is a magnesium-iron-tin borate of low tin content, being approximately 10 per cent Its occurrence so far has not warranted exploitation

TESTS FOR TIN

Although the most important tin mineral, cassiterite or tinstone, can generally be readily recognized in coarse grains or larger fragments because of its high specific gravity, its unusual hardness, color and adamantine luster, these physical characteristics are not sufficiently reliable in identification of the mineral when it occurs as small water-worn grains in alluvial deposits

A very useful field test for tinstone depends upon the fact that stannic oxide is readily cathodically reducible by hydrogen The field test consists of placing the grains in contact with zinc or iron in a solu-

tion of a cold dilute non-oxidizing mineral acid such as hydrochloric
or sulfuric The nascent hydrogen, evolved as a result of the action of
the acid on the zinc at the contact surface between the grain and the
metal, reduces the stannic oxide, leaving a very thin film of metallic
tin as a gray coating over the grains of the mineral If the small pieces
of the mineral be washed and then rubbed between the fingers or on
a piece of soft fabric, the bright unmistakable silver-white surface of
metallic tin is produced No other mineral is affected in a similar
manner by hydrogen reduction Jones[1] states that serious mistakes in-
volving considerable sums of money have been made from mistaking
grains of such minerals as wolframite, ilmenite, zinc blende, rutile,
zircon, tourmaline, garnet, hematite, etc, for tinstone Tinstone may
occur pseudomorphous with a number of minerals such as tantalite,
columbite, and rutile Table 4 (from Jones) shows the physical charac-
teristics of those minerals which may be taken for tinstone

TYPES AND GEOLOGY OF TIN DEPOSITS

Tinstone occurs in nature in two types of deposit, the first of a
primary nature, being veins, and the second of secondary origin as
alluvial or placer and detrital deposits Those not occurring in situ as
in veins are conveniently termed secondary stanniferous deposits
Jones[2] states

> By far the greatest amount of the world's supply of this mineral has been
> derived originally from stanniferous veins of quartz and pegmatite traversing
> granite, schists, phyllites and slates, and it is also derived from veins of aplite,
> quartz-porphyry, greisen and other granite modifications traversing the rocks
> named above, and occasionally in veins traversing quartzite, limestone and other
> rocks The term "granitic rocks" is conveniently used to embrace the quartz,
> pegmatite, aplite, quartz-porphyry, greisen, etc, which occur in veins or dykes,
> for they are modifications of granite, and represent the residual and more acid
> part of the parent granite magma Tinstone is also found disseminated through
> granite and adjacent rocks, but such occurrences are rarely workable as ore
> bodies, although they may have contributed a good deal of tinstone to neighboring
> secondary stanniferous deposits
> The bulk of the world's supply of tinstone is obtained at present from stan-
> niferous alluvial and eluvial deposits derived from mineralized areas in their
> immediate neighborhood It is an interesting and significant fact that *not in a
> single tinfield in the world has tinstone been found "in situ" except near granite
> or granitic rocks,* and it has not been found in alluvial or eluvial deposits except
> where these have been derived from mineralized areas in which granite or granitic
> rocks are known to occur

Tin as an element forms less than 0 001 per cent[3] of the igneous
rocks in the earth's crust Only a small fraction of the earth's granite
masses is stanniferous It is thought that there are no exceptions to

[1] "Tinfields of the World," Mining Publications, Ltd, London, 1925
[2] *Loc cit*
[3] F W Clarke and H S Washington, *U S Geol Survey, Prof Paper* No 127 (1924)

TABLE 4

MINERALS OFTEN MISTAKEN FOR TINSTONE

Mineral	Specific Gravity	Hardness	Crystal Form	Test
Tinstone, SnO_2 (cassiterite)	6 8 to 7 1	6 to 7	Tetragonal pyramids or prisms	See text
Zinc blende, ZnS	4 0	3 5	Cubic system, in tetrahedrons	The encrustation on charcoal when heated with cobalt nitrate, gives grass-green color Sulfuretted hydrogen evolved with hydrochloric acid
Ilmenite, $FeO\ TiO_2$	4 7	5 5	Tabular, trigonal	Gives a yellow solution with potassium bisulfate, which turns violet when reduced with tin
Wolframite, $(FeMn)WO_4$	7 5	5 5	Tabular crystals, monoclinic	Cleaves easily into thin flakes Fused mass is decomposed with hydrochloric acid and when heated with tin gives a blue solution
Hematite, Fe_2O_3	4 9 to 5 3	5 5 to 6 5	Rhombohedron, reniform, etc	Become magnetic on heating Red streak
Rutile, TiO_2	4 2	6 5	Like cassiterite	Fused with potassium bisulfate it gives a solution which when reduced with tin has a violet color
Zircon, ZrO_2SiO_2	4 7	7 5	Prisms with pyramids Tetragonal	Almost always shows good crystal forms
Tourmaline, Borosilicate of Al, etc	3 1	7 5	Prisms with pyramids Trigonal	Generally appears like an aggregate of black needle-like crystals Breaks easily, and can be panned off as easily almost as quartz grains
Garnet, $3R''\ OR_3''\ O_3\ 3SiO_2$	3 7 to 4 0	7 5	Dodecahedron Cubic	Can be panned off easily, being only a little more than half the weight of cassiterite
Axinite, Borosilicate of Al and Ca	3 3	6 5	Flat crystals Triclinic	Intumesces in blowpipe flame.
Tantalite (Columbite) Niobate and tantalate of iron and manganese	5 3 tc 7 3	6	Orthorhombic	Gives a dark-red to black powder and streak

the rule that primary tin deposits occur in or near an acid igneous rock such as granite or related rocks like granite-porphyry, quartz-prophyry, aplite, pegmatite, or quartz These rocks generally occur as veins traversing granite and metamorphosed rocks of sedimentary origin, as illustrated by schists, phyllites, slates, and quartzites, and metamorphosed limestone in some tinfields

While it is true that tinfields occur in connection with acid igneous rocks, the converse is not true, for there are extensive areas of granitic rocks which contain no tin minerals In Pahang in the Federated Malay States, the Benom and the Main Range of the Peninsula run approximately parallel, only about twelve miles apart Tin mining is extensively done in the Main Range, while the Benom Range has failed to show the existence of any tin deposits in it Mica, muscovite, and lepidolite are abundant in the Main Range but absent in the Benom chain, while hornblende, widely distributed in the Benom granite, is rare in the Main Range

The economically important primary tin deposits occur in the infillings of fissures It is thought the position and shape of the veins were determined by pre-existing fissures which were enlarged as they became infilled with magma under pressure The fissures probably occurred during the later consolidation phases of the granite magma When formed, they were filled with the residual and more acid differentiation products of the parent magma during the final stages of the igneous intrusion Mineralizing gases and carriers for tin and other metals, such as borates, fluorides, sulfides, arsenical compounds and related products in the residual magma, probably formed the metalliferous compounds and the related minerals now found in the veins resulting from the fissure infilling Most authorities agree that the carriers of tin minerals were in the gaseous state A minority, however, believe that mineralizing liquids played the more important part The magma must have been in a very fluid state during its intrusion into the fissures as well as under very great pressure The cause of this pressure is a debatable question even today among our geologists

Stanniferous veins are generally more common on the margins of granite masses where the fissuring is more pronounced The greater portion of the world's supply of tin minerals is obtained from granite contact lodes

The discussion of tinfields will be subdivided into what are now considered the various metallogenetic tin provinces,[4] or the areas where primary tin deposits were formed at the same period of mineralization

[4] Rastall, "Geology of the Metalliferous Deposits," Cambridge University Press, 1923

Chronologically in respect to their discovery and working on a considerable commercial scale, these are the tinfields of (1) the west of England, Brittany, and the Erzgebirge, (2) Burma, Siam, the Malay States, and the Dutch East Indies, (3) Bolivia, (4) Nigeria, and (5) Australasia, in reference to which it is not certain that all the tinfields there may be grouped in one province

THE EUROPEAN METALLOGENETIC TIN PROVINCE

Rastall points out that the tinfields of the west of England and of Brittany form detached portions of a single geological unit, while the tinfields of Saxony and Bohemia in the Erzgebirge are of a very similar type belonging to the great mountain systems of Central Europe The tinfields of Portugal and Spain form part of an ancient plateau consisting of paleozoic rocks strongly folded by the same type of convulsions as gave rise to the geological units in Brittany and the Erzgebirge
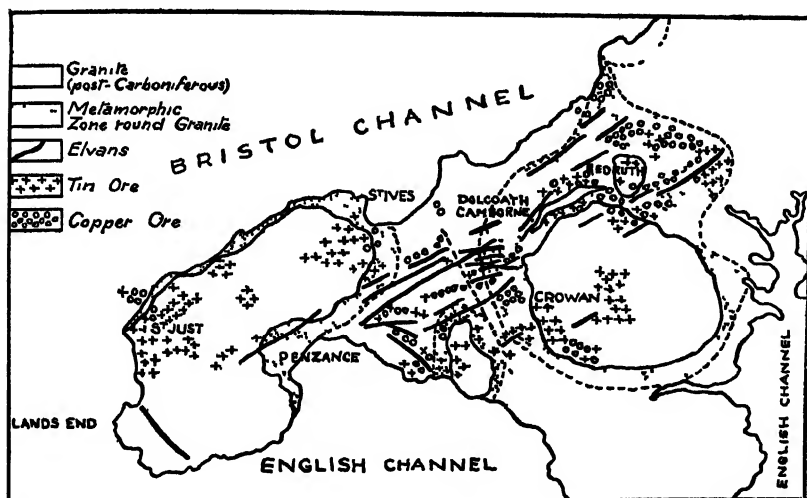
Fig 14—Geological map of West Cornwall showing the relation of the ores to the granite (Jones)

Cornwall is now practically the only source of tinstone in Great Britain and Ireland, although a small amount comes from that part of the mineralized area which extends into Devonshire The history of tin mining in Cornwall dates back to prehistoric times The mineralized areas are either in the granite or on the margins of the granite, or in the metamorphosed sedimentaries nearby Nearly all of the tin ore in

Cornwall and Devon occurs in lodes in the infillings of fissures in the granite and in the adjacent sedimentaries At times the country rock may be extensively altered, making it impossible to distinguish the walls of the lode In certain sections of Cornwall, particularly at East Pool, no normal granite is seen except at a considerable distance from the lode, as a result of silicification Such alteration is also very common in parts of the Malay Peninsula Irregular bunches or masses of ore may occur where the lode widens out

The relation of the Cornwall tin mines to the granite is shown in Figure 14 The minerals are distributed vertically in the tinfields with a certain regularity Jones believes that "there is sufficient accumulated evidence to point very strongly to the conclusion that such distribution is intimately related to the temperatures and pressures of formation of these minerals Those of the highest temperature of formation, like tinstone, occur towards the bottom of the metalliferous depth zones " Figure 15 shows the vertical distribution of mineral zones in Cornwall as given by Dewey [5]

The highly mineralized area of Camborne and Redruth produces about 95 per cent of the total output of Cornwall Tin and copper minerals were probably obtained from Land's End during the Bronze Age In 1907 all alluvial working for stream tin ceased, and only a few tin and copper mines have worked intermittently since There is a rich group of copper and tin lodes in the parish of St Just and a smaller group near St Ives, both close to the northern margin of the Land's End granite

No economically important deposits of tinstone occur in Scotland, Ireland, France, or Holland

Situated in the same metallogenetic province are the Erzgebirge tin deposits in Czecho-Slovakia and Germany These deposits have been worked for tinstone for the last eight centuries The principal rocks of the highlands extending along the boundary of Saxony and Bohemia are gneisses, schists, and phyllites At present tinstone is mined in the Altenberg-Zinnwald district, at Sadisdorf, Altenberg, Zinnwald, and Graupen The workings at Altenberg are confined to the small granite stock intrusive in granite-porphyry and traversed in different directions by innumerable minute stringers of tinstone so thin as to be almost invisible. The adjacent rock is mineralized The percentage of tin in the rock varies from 0 1 to 0 9 per cent, with an average of 0 3 per cent, carrying a bismuth content of 0 002 per cent It is only because of the peculiarly favorable conditions that it is possible to work the deposit
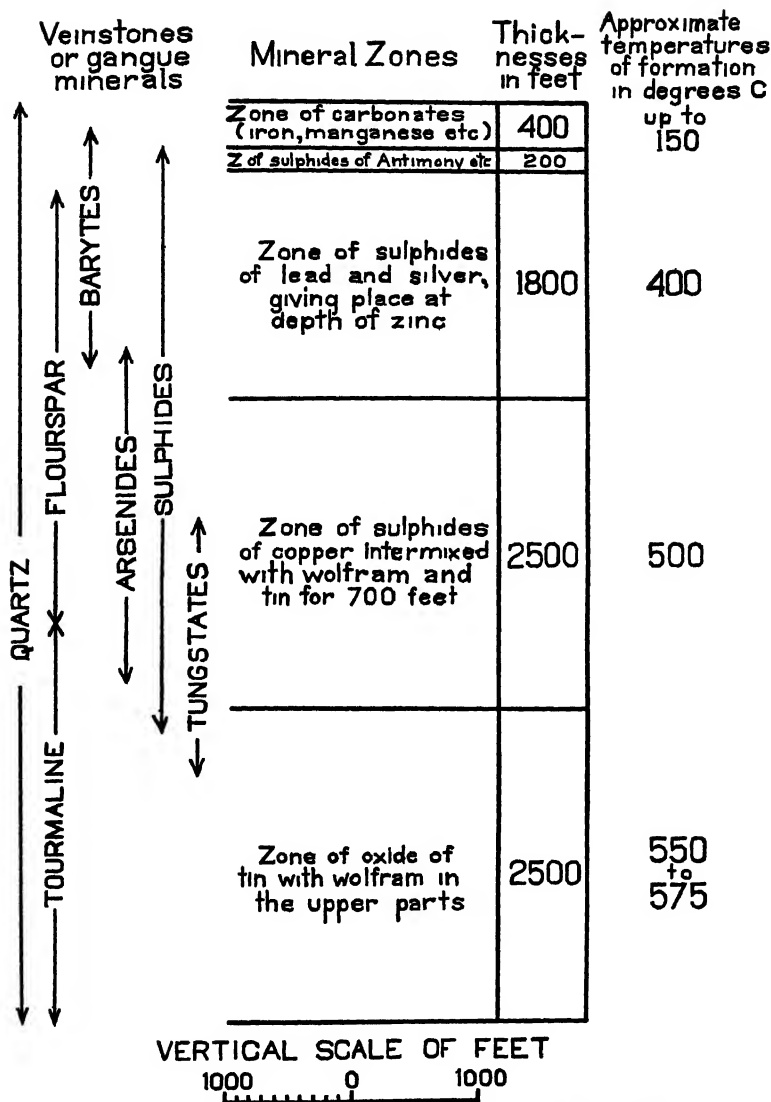
[5] Pres Address, Geol Assoc , Feb 1925, p 129

Veinstones or gangue minerals	Mineral Zones	Thicknesses in feet	Approximate temperatures of formation in degrees C
	Zone of carbonates (iron, manganese etc)	400	up to 150
	Z of sulphides of Antimony etc	200	
	Zone of sulphides of lead and silver, giving place at depth of zinc	1800	400
	Zone of sulphides of copper intermixed with wolfram and tin for 700 feet	2500	500
	Zone of oxide of tin with wolfram in the upper parts	2500	550 to 575

QUARTZ

FLOURSPAR

TOURMALINE

BARYTES

ARSENIDES

SULPHIDES

TUNGSTATES

VERTICAL SCALE OF FEET

1000   0   1000

FIG 15—Diagram showing the vertical distribution of mineral zones in Cornwall

profitably The Erzgebirge deposits are more important historically than as tinstone producers

Associated with wolframite, tinstone occurs in a mineralized belt extending with numerous breaks from the northwest of Galicia in northwest Spain through the provinces of Pontevedra and Orense to

the northeast of Portugal, and as far southwards as the mountain ranges
Sierra da Estrella The position of the chief tin and tin-tungsten fields
in Spain and Portugal is given in Figure 16 These fields belong to the
same metallogenetic province as those of Cornwall, Saxony, and
Bohemia   Spain at present produces very little tinstone, the average
being about 20 tons in terms of metallic tin per year Practically the
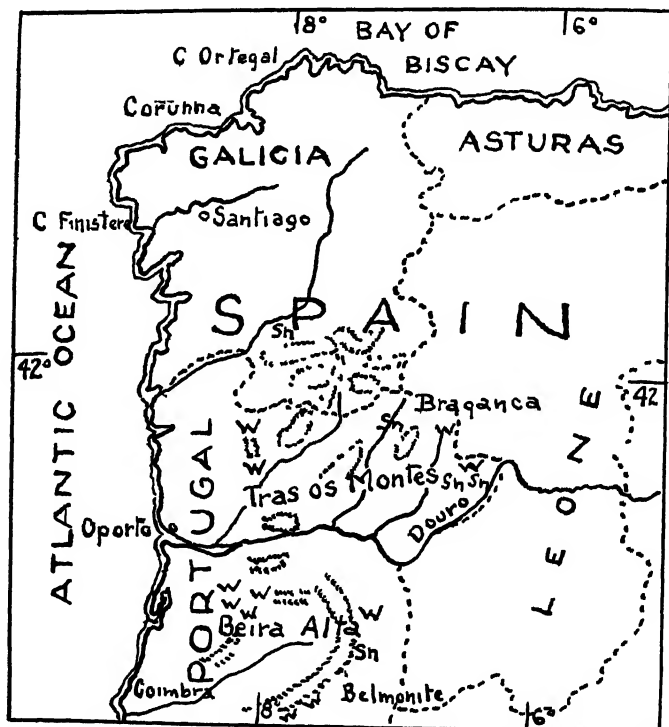
FIG 16 —Map showing the chief tin and tin-tungsten fields in Spain and Portugal
(Jones)

whole Portugal output, about 400 tons a year, comes from shallow
stanniferous alluvial deposits in the Gaia Valley near Belmonte

Italy has no important tinstone deposits

While it is known that tinstone occurs in the Trans-Baikal province,
in the Urals, in the Russian Empire, and in Finland, only a portion
of the deposits have been worked on a small scale At Pitkaranta in
Finland veins traversing metamorphosed limestone and schist have been
worked for iron and copper ore, tinstone, and silver Their present pro-
duction is exceedingly small

Fig 17 —Map showing tinstone-wolframite fields of Malaya, Dutch East Indies, Siam, Burma, and the Yunnan fields of China (Jones)

THE ASIATIC METALLOGENETIC PROVINCE

The chief tin-producing part of Asia is a mineralized belt which is continuous through Lower Burma, Lower Siam, the Malay States into the islands of Singkep, Banka and Billiton in the Dutch East Indies This intensively mineralized metallogenetic tin province produces more than 60 per cent of the world's total annual production The location of the fields is given in Figure 17

Tin mining is in operation in every one of the Federated Malay States—Perak, Selangor, Negri Sembilan, Pahang—and each of the

FIG 18—The irregular limestone floor of a mine at Siputeh, Kinta
(Courtesy Geological Survey, Federated Malay States)

Unfederated Malay States—Kedah, Perlis, Kelantan, Trengganu, and Johore So extensive is the mineralization in and near the granite of the Peninsula that it is stated that it would be difficult to find any stream having its source in the Main Mountain Range that did not contain in its bed a certain amount of tinstone For a long period of years, Perak has remained the chief tin-producing state in British Malaya, being responsible for more than 65 per cent of the total output of the country, or about 20 per cent of the world's total production The Kinta district in the center of the state is the chief producer A typical mine in this region is shown in Figure 18 This district, only 36 miles long and 25 miles wide in its maximum width, is estimated to be the source of about 50 per cent of the British Malaya's output This small area produces about as much as Siam, China, and Nigeria together In the

Gopeng Consolidated Mines in the Kinta district, the detrital deposits worked carry 1 25 to 1 4 pounds of tinstone to the cubic yard, while in the mines of the South Perak Tin Dredging Company the alluvial deposits handled carry about 0 73 pound of tinstone to the cubic yard

The alluvial and residual placers of the Malayan deposits account for 94 per cent of the total output Of the remaining 6 per cent, the Pahang Consolidated Company, Ltd, produces nearly all of it from lode mining The placers are on the west side of the Peninsula, covering large areas, and are virtually continuous for some 200 miles The
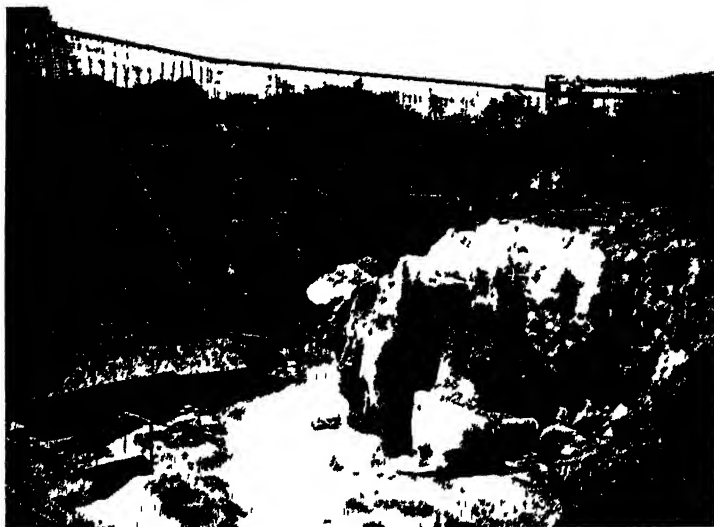
FIG 19 —A mine near Lahat
(Courtesy Geological Survey, Federated Malay States)

richest of the placer deposits are of the residual type and are known as "contact mines " Dredging, begun in 1912, has increased until it now accounts for upwards of 20 per cent of the total production The ground has been carefully prospected and the richest spots mined The ground now available for dredging consists of old Chinese tailings too low to work by hand methods It is thought that areas set aside for agriculture contain valuable placers In the Gopeng mine the deposits consist of decomposed schists and phyllites, varying in thickness from about 50 to over 120 feet, that have in many places become disorganized due to their subsidence on the metamorphosed underlying limestone There are many extremely large open-cast workings The Tronoh mine in the western part of the Kinta district formerly obtained the bulk of its tinstone from an enormously large open-cast mine at the foot of a

hill composed of schists, granite and granitic intrusions The limestone rock at the foot of the hill had been dissolved to form a trough about 1,900 feet long, 500 feet wide, and about 150 feet deep As this trough was being formed, the eluvial deposits on the steep flanks of the hill kept slipping down Stanniferous eluvial and alluvial deposits to the extent of about four million cubic yards occurred in the trough The sinking movement had caused concentration of the tinstone in exceedingly rich patches When Tronoh Mines was the largest producer of tinstone of the world, no machinery of any kind except for pumping

Fig 20 —The North Mine in Lahat Ltd's property, in 1921
(Courtesy Geological Survey, Federated Malay States)

water was employed The mine was worked by thousands of Chinese coolies who carried the tin-bearing ground to the surface in baskets suspended from shoulder sticks Formerly, under certain circumstances, many mines in the Malay Peninsula could be worked more economically by hand labor than by machinery Tin mining in loose ground, however, has been revolutionized in recent years by the use of gravel pumps and bucket and suction cutter dredges

The state of Selangor produces about 25 per cent of the total output of the Federated Malay States The geological structure of the tin-mining areas is very similar to that previously described in the Kinta district. In South Selangor tinstone in situ has been worked on a small scale in hundreds of places in the foothills. The decomposed surfaces

of the mineralized granite, schists, and phyllites have been removed and the mineral recovered in sluice boxes after hydraulicking

Some of the Malay mines are shown in Figures 19 and 20 In Figure 19, the large mass of rock on the right of the picture is crystallized limestone

In Figure 21, the cap of the tin-bearing pipe is shown shortly after it had been uncovered Figure 22 shows this extraordinarily rich tin-bearing pipe in the crystalline limestone It is now worked to the depth of several hundred feet

FIG 21 —The Beatrice Mine in September, 1923
(Courtesy Geological Survey, Federated Malay States)

It is a popular belief in the United States and Europe that there are many large tin mines in the Straits Settlements "Straits tin" is known the world over People who are not interested in mining have taken it for granted that Straits tin is mined in the Straits Settlements The total amount of tinstone mined in the Straits Settlements, however, would form only a very small fraction of the output of even one of the smaller tin mines in the Malay States Practically the whole output of tinstone concentrates from the Malay States is smelted at Singapore and Penang in the Straits Settlements The two largest tin-smelting companies in the world are the Straits Trading Company at Singapore and Penang, and its subsidiary, the Eastern Smelting Company at

Penang Tin mining on a very small scale has been carried on in
Malacca and at times in the Dindings

Almost the entire production of tinstone in Siam comes from the
western side of that narrow part of the country lying between Lower
Burma and the Malay States, where it forms part of the Malay Pe-
ninsula The tinfields of Siam form part of the mineralized belt that
runs parallel to the granite ranges previously described as continuous

FIG 22 —The Beatrice Mine, near Ipoh, in 1925
(Courtesy Geological Survey, Federated Malay States)

through Lower Burma, Lower Siam, the Malay States, and the Dutch
East Indies Stanniferous alluvial deposits are worked by bucket dredg-
ing in the neighborhood of Renong and as far southward as the island
of Puket, about half-way between Victoria Point, Lower Burma, and
the northern boundary of the state of Kedah in the Malay States
Here the Tongkah Harbor Tin Dredging Company works stanniferous
alluvial deposits in the shallow harbor of Tongkah The dredges work
from near the shore to a few miles out at sea Here the shallow water
covers a coarse sand containing well-rounded grains of tinstone derived

from the mineralized area forming the seashore Jones [6] states that part of the flatland on the shore had been worked When he visited the place the main street of the small town of Tongkah had also been dredged

Almost all the tin mines in the Indian Empire are restricted to Lower Burma where the chief producing centers at present are in the Tavoy and the Mergui districts Here the stanniferous areas are worked by bucket dredging and gravel pumps The deposits are largely alluvial The tin and tungsten localities in Burma are shown in Figure 23 In the Tavoy district all but a few of the mines produce mixed wolframite-tinstone concentrates varying in their tin content from below 1 per cent tin and over 70 per cent WO_4 to those carrying over 20 per cent tin and in exceptional cases to well over 40 per cent No wolframite chemically free from tin is known to occur in the whole district The Tavoy Tin Dredging Company works the chief alluvial stanniferous deposit at Hindu Chaung The average yield of recent years has been 1 21 pounds of tinstone per cubic yard

The Dutch East Indies contribute about 23 per cent or more of the world's supply of tin The continuation of the mineralized belt of the Malay States extends through the islands of Singkep, Banka, and Billiton in the Dutch East Indies For a long period of years these small islands have alternated with Bolivia as the second largest tin-producing areas Whereas almost the whole of the Bolivian yield is obtained from lode mining, practically the total output of the Dutch East Indies is from alluvial and detrital deposits The island of Banka produces about two-thirds of the tin shipped from the Dutch East Indies, and Billiton nearly all the remainder, with the exception of about 2 5 per cent from Singkep Banka's production is about as large as the combined outputs of Siam, China, and Nigeria The Billiton and Singkep areas contain considerable reserves but their total is probably only a fraction of those of Banka The deposits are owned by the Government of the Dutch East Indies The tinstone concentrates are very high grade The impurities have been decomposed and removed by percolating waters They therefore offer no difficulty in smelting and refining the metal The deposits have been derived from the weathering down of the mineralized areas in granite and in schists and phyllites near the granite margins

No tinstone deposits of importance occur in Sumatra The only important deposits of tin in French Indo-China are in association with wolframite in the provinces of Tonkin and Laos Decomposed stock

[6] *Loc cit*

works and detrital deposits are worked open-cast   When a plentiful
supply of water is available during the rainy season, the rich deposits
yield large profits   The most important alluvial deposits are those at
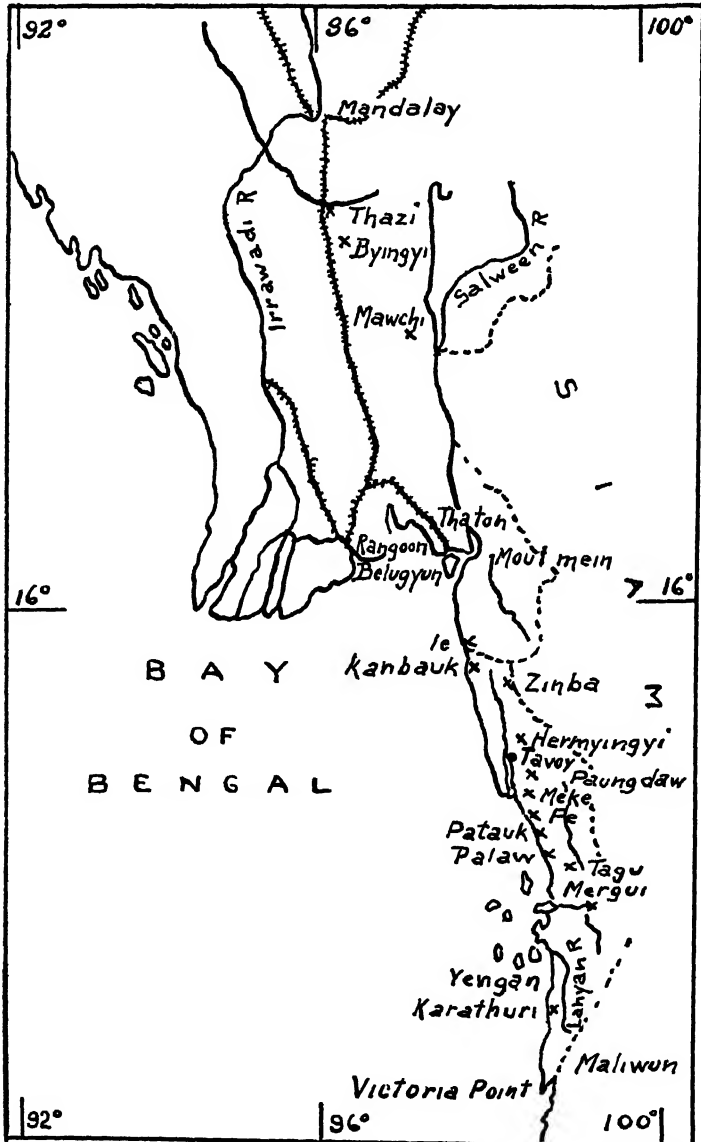Beau-Site and St Adele

Fig 23 —Map showing tin and tungsten localities in Burma (Jones)

Tinstone is known to occur in the Chinese provinces of Yunnan, Kwangsi, Hunan, Kwangtung, and Fukien The tinfields extend over large areas The chief producing center is about thirty miles west of the treaty town Mengtze in Yunnan About 93 per cent of the total production of China comes from Yunnan, 4 per cent from Kwangsi, and 3 per cent from Hunan The tinstone occurs in alluvial deposits in large solution cups and troughs resting on a limestone bedrock The

FIG 24 —Chinese mine at Kongsi
(Courtesy Malay States Information Agency)

alluvium is of a dark-brown argillaceous nature, highly ferruginous Jones [7] states that the deposits appear to be similar to certain stanniferous alluvial workings in the Malay States The mining methods in operation are primitive in the extreme No machinery of any kind other than native pumps worked by hand or by foot is used The overburden is dug out manually and carried to the surface in shoulder-stick baskets where the tinstone is concentrated in small sluice boxes Many of the mines in the Hunan and Kwangsi Provinces, such as shown in Figure 24, are small and are worked by native labor In the Fu Chuan district the tin deposits are all alluvial and detrital, scattered over a

[7] *Loc cit*

granite range for a distance of thirty miles The ground worked carries
about 3 pounds of tinstone per cubic yard Very little tin is produced in
the Kwangtung and Fukien Provinces, although tinstone is known to
occur there

Tinstone is mined in Satsuma Province in Japan, where it occurs in
quartz veins intrusive in metamorphosed sedimentaries, phyllites, and
slates Some of the lodes carry as high as 3 per cent tin Stanniferous
alluvial deposits are known to occur in the vicinity of Takayama and
Hirukawa in Mino Province, where the stanniferous gravels occur as
beds on the river banks

The Bolivian Metallogenetic Tin Province

While in the Malay States, Dutch East Indies, Siam, China, and
Nigeria the bulk of the production is obtained from stanniferous
alluvial and detrital deposits, practically all the Bolivian tinstone pro-
duction is from primary or vein deposits For the period between 1905
and 1920 Bolivia was second only to the Federated Malay States as
a tin-producing area It was second again in 1922 but third in 1923,
being superseded by the Dutch East Indies Bolivia produces from 22
to 25 per cent of the world's tin production The mineralized areas of
Bolivia consist of a high plateau or table land nearly 500 miles long
and over 100 miles wide, about 12,500 feet above sea level The tin
mines are at elevations of about 12,000 to nearly 20,000 feet, mines
at the higher elevations being in a rugged, snow-clad country where con-
ditions are severe The chief tin-mining centers are shown in Figure
25 The tinstone deposits are the most widely distributed of all the
mineral wealth of Bolivia They are worked throughout the extent of
the Cordillera Real Mountains and their southern extension from the
north of La Paz to the southeastern end of the department of Potosi
About 90 per cent of the total production comes from ten producing
centers and no less than 40 per cent of the total output is from mines
at Uncia and Huanuni Tin mining in Bolivia is of comparatively
recent origin, although the tin deposits have been known for several
hundred years At present little if any tin is obtained from placers, but
this class of mining is now being developed Furness[8] states that
approximately 70 per cent of the tin production of Bolivia comes from
the Llallagua and La Salvadora mines of the Patiño Company The
mineralized area containing tin is large Development work has been
confined to the accessible localities. The output of many mines is limited
to extremely high-grade ores in order to meet transportation charges

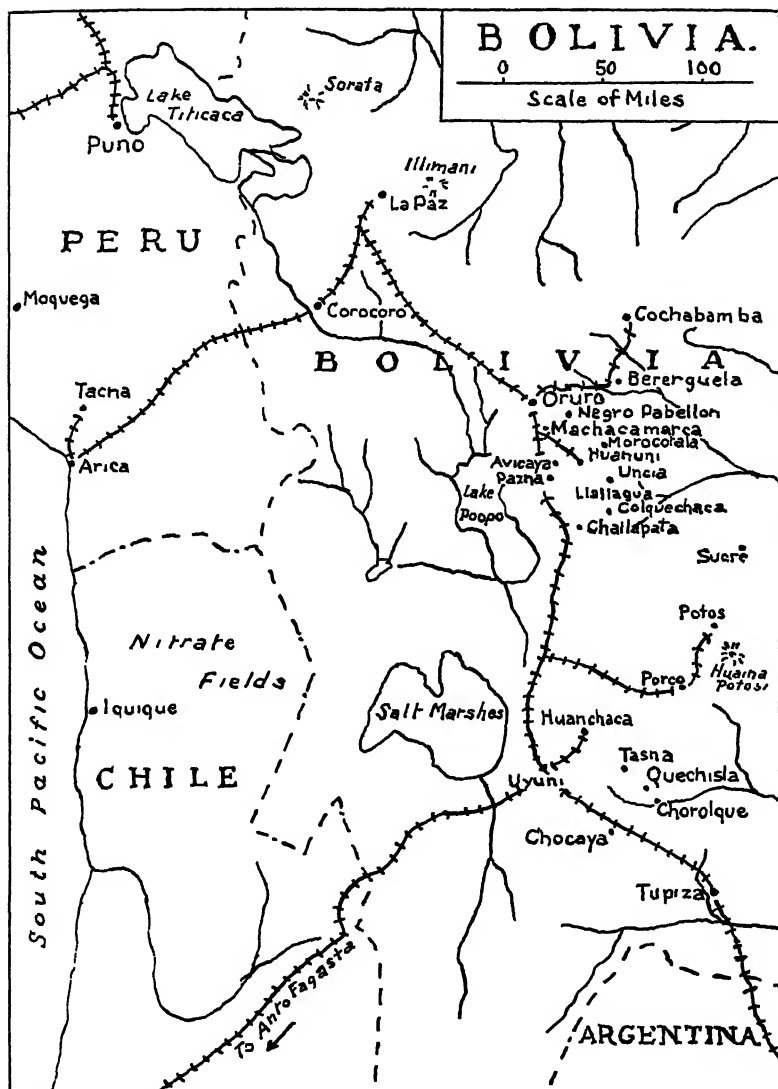[8] U S Geological Survey, "Mineral Resources of the United States," 1925, Part I, Tin

FIG 25 —Map showing chief mining centers in Bolivia

From the character of the deposits in the accessible localities it seems fair to assume there are relatively large bodies of low-grade ore which will become productive when transportation facilities are improved Because of the topography of the tin-bearing areas, the development of adequate transportation will probably be very gradual

The ten most important producing centers from north to south are Araca, Oruro, Machacamarca, Huanuni, Llallagua, Uncia, Potosi, Sala Sala, Chocaya, and Chorolque The most important of these is the department of Potosi, which produces about half of the Bolivian output The type of country in Potosi is shown in Figure 26 Davy [9] states that the mines of Milluni, Huayna, Potosi, Araca, Choquetanga, San Enrique, Mallochuma, Quimsa Cruz, and Santa Vela Cruz are grouped along the west and south border of the granite area All the rest, including Oruro, Negro Pabellon, Llallagua, Uncia, Avicaya, Potosi, Porco, Pulacayo and many others, are found in or about intrusions of
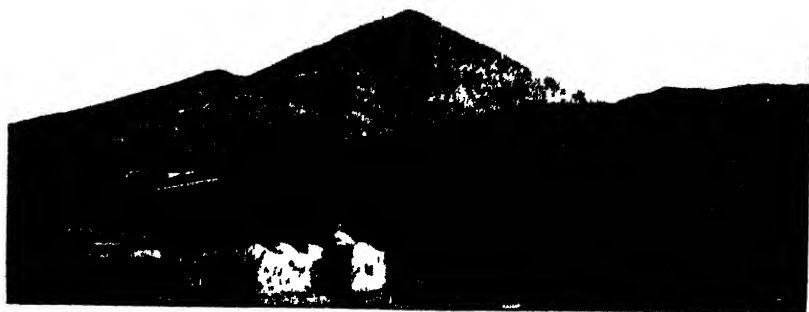
Fig 26—The Potosi tin area in Bolivia

quartz-porphyry or related types of acid igneous rocks, with the exception of one or two occurrences where the workings have not, so far, exposed igneous intrusions Granite outcrops in small areas near Potosi and may be at no great depths beneath the surface in many other places, especially in the vicinity of Uncia, Llallagua, and Avicaya, where the deposits have similarities to the Bolivian tin deposits in or about the granite itself Although the silver veins worked at Potosi carried tinstone, the old Spanish miners rejected it as rubbish Its value was not recognized until about the middle of last century when it was first mined at Huanuni, in Oruro, and smelted in small charcoal furnaces similar to those which are still used in some of the tin-mining areas A tin mine near Oruro is shown in Figure 27

⁹ "Ore Deposition in the Bolivian Tin Silver Deposits," *Econ Geol*, 15 463 (1920)

The Uncia group became the largest tin-producing mines in the world in 1912 with a monthly production of about 900 tons of high-grade tinstone concentrates With the piesent production of 700 tons a month, it is second only to the adjoining Llallagua Company's mine Since 1913 the Llallagua mine has been the largest producer of tinstone in the world, with an output of about 1,300 tons a month of concentrates carrying 70 per cent tin metal Bismuth is produced as a by-product The grade of the oie worked is about 9 per cent tin Jones states that the cost of production varies in most mines about £50 to £70 ($240 to $330) per ton of 60 to 70 per cent tinstone concentrates at

FIG 27 —Tin mine near Oruro, Bolivia

the mine The average grade of ore milled is probably at present about 6 per cent metallic tin, with a tendency toward a lower figure with the metal at a high price Labor in all but the highest grades is almost entirely native—that is, either Mestizo or Indian The rates of pay for a miner vary from 2 50 to 6 00 bolivianos (1 boliviano = 38 93 cents, par value) per day, and for laborers 1 80 to 4 00 bolivianos Venables and Howard-Wright [10] state that the efficiency of the miners and laborers is moderate The labor supply varies much in different parts of the country

Chile and Peru produce very little tinstone, although they export large quantities of the mineial which has been mined in Bolivia Tinstone deposits in Peru are known to exist

[10] "Mining in Bolivia," *Mining Mag*, 31 2⁻⁻ (1924)

The Nigerian Metallogenetic Tin Province

Nigeria now produces approximately 5 per cent of the world's tin production The occurrence of tinstone and smelting methods were known to the natives in Western Bauchi in Nigeria before European occupation The tin deposits are distributed over an extremely extensive area, well over 10,000 square miles The most important deposits, however, occur in Bauchi Province The bulk of the output of tinstone in Nigeria is from secondary stanniferous deposits These alluvial and detrital deposits are of varied types due to the different conditions during different geologic times under which they were formed Some accumulated before the elevation of the plateau in which they are found and have remained in their original area of deposition Others have been removed and redeposited by streams forming and reforming and changing their channels Still other deposits result from the denudation of part of the ore bodies after the uplifting of the plateau These are now found in the present river beds and the flats on the river banks Hollows or pockets filled with rich stanniferous gravels frequently occur in the channels of the rocky streams Sharp angular tinstone in quantities of economic importance frequently occurs on the weathered outcrops of stanniferous quartz, pegmatite veins, and other mineralized rocks Falconer [11] states that the minerals most commonly associated are topaz, ilmenite, magnetite, rutile, zircon, monazite, garnet, and more rarely, columbite, wolframite, corundum, and gold Raeburn [12] considers the important stanniferous terrace deposits at Jemaa as alluvium deposited by the river which has subsequently eroded its bed Tinstone occurs free from impurities when concentrated Stream-bed deposits are widely distributed over Nassarawa The tinstone here has been derived from weathered mineralized granite

One of the chief factors which limits Nigerian production is a small quantity of water during most of the year, water being exceedingly important in the working of the secondary deposits by the usual methods

No deposits of value have as yet been found either in the Gold Coast or Nyasaland

Practically the whole output of tinstone of the Belgian Congo comes from a mineralized belt about 250 miles long in Katanga on the northwest face of the rugged plateau of Monte Mitumba The mountains are composed of mica schists, tourmaline-bearing quartzites, and slates The tinstone occurs in quartz and pegmatite veins in detrital and

[11] *Geol Survey of Nigeria, Bull* No 1, 1921
[12] "The Tinfields of Nassarawa," *Geol Survey of Nigeria, Bull* No 5, 1924

alluvial deposits The greater portion of the output has so far been obtained from shallow alluvial and detrital deposits

No tinstone deposits have been worked in Portuguese East Africa Only one company has been successful in working the detrital deposits in Southwest Africa Here the tinstone is sporadically scattered through pegmatite in large grains and crystalline masses

Rhodesia produces no tinstone concentrates, although a number of veins and alluvial deposits are known

In the Union of South Africa there are many ancient workings in places in the Transvaal where tinstone was formerly smelted by the natives The Cape Province, Transvaal and Swaziland outside of the Union now produce tinstone concentrates Cassiterite is known to occur in Natal, but no important deposits have been so far discovered The Transvaal tinfields are those of the Waterberg in the northwest and the eastern Transvaal tinfields near the borders of Swaziland They are secondary stanniferous deposits derived from the many large pegmatite veins traversing the granite The tinfields occupy the eastern and southern margins of a geological basin, the central portion of which is composed of sandstones and conglomerates Feldspar is frequently and intimately associated with the cassiterite in red granite

The Australasian Metallogenetic Tin Province

Jones [18] states that it is doubtful whether the tin deposits of Australasia may be grouped together in one metallogenetic province Tin is known to occur in various parts of the Australian continent, in Tasmania and in New Zealand Of the Australian States, Victoria has the lowest and New South Wales the highest output All together the total production of Australasia is 2 to 3 per cent of the world's production

The geographic distribution of cassiterite in New South Wales is very wide By far the most important tinfields are those in the neighborhood of Emmaville and Tingha Here it occurs in lodes, in stock works, and alluvial deposits The chief tinfields of New South Wales, Queensland, Victoria, Western Australia, and Northern Territory are shown in Figure 28 By far the greatest bulk from the Tingha district is from alluvial deposits In many sections of Australia the lack of water is a decided handicap in mining stanniferous gravels One of the best known mines is that of Mt Bischoff in northern Tasmania This unit, however, is more of historic interest than of present-day importance, inasmuch as the known residual deposits are approaching exhaustion No large lode mines are known in Australia and there is little interest

[18] *Loc cit*

FIG 28—Map showing the chief tinfields of New South Wales, Queensland, Victoria, Western Australia, and Northern Territory

in such working The most important tinfield in Queensland is the Herberton, its production in 1923 being about one-third from lode mining and two-thirds from alluvial gravels Cameron [14] states that the greater part of the lodes traverse coarse graywackes [15] and quartzites The granite is a biotite granite and in places a hornblende granite Occasionally tinstone occurs in grains disseminated through the unaltered granite and porphyry The associated minerals are topaz, fluorite, tourmaline, and in some lodes wolframite, bismuthine, antimonite, galena, and chalcopyrite

The chief mineralized areas of Victoria are in the northeastern part of the state Tasmania has been for the last seventy-five years one of the chief producers of tin in Australasia and in recent years had a larger output than any of the states The greater part of the tinfields are confined to the northern half of the island It is interesting to note that Tasmania claims to have produced the largest individual mass of tinstone known Three-fourths of the whole mass of the Gormanstown nugget, which weighs about 1,900 pounds, is claimed to be tinstone The most interesting mine in Tasmania is that of Mt Bischoff Situated toward the top and on the flanks of a mountain about 2,600 feet high, it is worked as an open quarry Lodes of the usual type occur, traversing quartz porphyry and slate The Queen lode varies from 8 inches to 18 feet in width and has been traced for a length of over 3,000 feet along its strike at an average width of 3 feet It is said to carry between 1 and 2 per cent of tinstone over a considerable distance Stanniferous alluvial deposits have been worked at Cox Bight in the southern division of Tasmania In the western division of Tasmania transport is a very serious difficulty, as it costs sixty to eighty dollars per ton of freight from Renison Bell on the Emu Bay Railway to the Stanley River fields

No stanniferous deposits of economic importance have ever been discovered in South Australia, and the occurrence of cassiterite in New Zealand is only of scientific interest

DEPOSITS UNRELATED TO ANY METALLOGENETIC TIN PROVINCE

Tin mining has been conducted in Mexico since the Aztec period The mineral was smelted by the Indians on a small scale before the advent of the Spaniards Tinstone is widely distributed, being found in the states of Durango, Jalisco, Guanajuato, San Luis Potosi, Queretaro, Aguas Calientes, Coahuila, and Sonora It occurs in veins traversing

[14] Report on the Herberton Tinfields, Department of Mines, Queensland (1904)
[15] Sandstone, usually of gray color, containing particles of other rocks and minerals in addition to quartz and feldspar

rhyolites with porphyritic quartz and feldspai It is often found dis-
seminated through the country rock in the neighboihood of the veins
Tinstone is often found in the form of wood tin Nodules weighing as
much as 25 pounds with decidedly radiating structure have been found
The associated minerals are chalcedony, opal, calcite, iron, and man-
ganese oxides, fluorite, topaz, wolframite, and bismuth mineials Stan-
niferous alluvial and detrital deposits occur in Aguas Calientes They
are very limited in extent

Promising occurrences of cassiteiite have been found in British
Honduras The deposits appear to have been derived from a mineralized
area of granite ranges At the present time the deposits are not of
economic importance

TINSTONE IN THE UNITED STATES

Tinstone has been found in many of the states of the United States,
but in no locality in paying quantities Prospectors in western parts of
the country have stated that cassiteiite is often found in the mountain
stream gravels California at one time pioduced small amounts of tin-
stone Cassiterite occurs in nariow quartz veins and as ieplacements
of granite in Virginia The ore bodies have been found disappointing
in both size and metallic content Periodically reports are ieceived of
"tin mines" in North and South Carolina The tin areas have been
examined by the United States Government, which ieported that "the
conclusion is irresistible that tin ore does not exist in this belt in suffi-
cient quantities to permit of a commercially successful opeiation"
Very small amounts of cassiterite have been mined fiom veins and
disseminations in granite in Texas and smelted locally

Hess [18] states that there are tin deposits in the Black Hills of South
Dakota, occurring in pegmatites and in quartz They occur in shoots
and are nowhere equally disseminated The shoots of profitable tin-
bearing rock are ordinarily of small cross section and of uncertain
length and depth Their occurrence in narrow dykes necessarily means
that in general they can be worked only on a small scale at each place
It was reported at one time that the National Tin Corporation in the
Black Hills had struck an ore body containing 2 per cent of tinstone
Operations have since been suspended

Stanniferous alluvial deposits were discovered in New Mexico in
1918 None of them proved to be of commercial value

Wood tin was found in 1916 in North Lander County, Nevada, in

18 "Tin, Tungsten and Tantalum Deposits of South Dakota," *U S Geol Survey Bull*, No
380, pp 131 63

narrow veinlets associated with specular hematite, chalcedony, quartzite, and tridymite Its occurrence was purely of scientific interest

Occurrences of tin of academic interest have also been found in Alabama, Connecticut, Georgia, Idaho, Maine, Massachusetts, New Hampshire, Washington, and Wyoming

Practically the only commercial production of tin from the United States and its territories is from Alaska where cassiterite grains are recovered incidentally to hydraulic gold mining and dredging The known tin deposits of Alaska indicating any future importance are situated in the extreme western part of Seward Peninsula Ear Mountain, Buck Creek, Cape Mountain, and Lost River have been mined for tinstone on a small scale The tinstone occurs in small veins and in alluvial deposits At the present time, production and tin mining itself are so small as to be merely interesting

Cassiterite occurs in a few places in Canada but none of the occurrences is of economic value In Lunenburg County, Nova Scotia, the mineral occurs in a quartz vein traversing granite, associated with chalcopyrite, wolframite, and zinc blende It has also been reported as occurring in granular quartz schists in some localities in British Columbia Microscopic crystals have been found in the gneisses of the graphite area of the Buckingham district

The North American continent to date has shown no tin-bearing mineralized areas upon which we may look as a future source of tin

CHAPTER 5

MINING AND ORE-DRESSING

OPEN-CUT MINING

Detrital deposits on hillsides are the most easily and cheaply worked sources of tinstone when sufficient water is available and where mine tailings can be readily disposed of into lower-lying areas Ground sluicing shifts the loose stanniferous deposits into trenches where the swiftly flowing water carries away the lighter materials, leaving the heavier minerals behind It is practised in some mines situated on steep hillsides in Malaya, Siam, the Dutch East Indies, and Nigeria Ground sluicing in a modified form is used in many mines to break up the ground, allowing it to float to lower levels from whence it is elevated by gravel pumps or by hydraulic lifts In very steep places the ground is broken into steps The water is made to run in shallow trenches dug at various heights in the working face It is desired to make as much use as possible of the water and the force of gravity Low-grade deposits cannot be worked economically by any other method It may be profitably handled by laborers working on hillsides where the rock is decomposed to the depth of several feet With a plentiful supply of water, a coolie will shift several cubic yards a day Damage is always done by the mine tailings

When cassiterite occurs in loose ground or in gravel free from much clay, panning is sometimes used to concentrate the mineral The pan is a large rounded shallow dish, frequently made of wood, in which, by a swirling movement, water is made to carry away the lighter minerals The method has the advantage that it is simple and can be applied where alluvial deposits are small or sparsely distributed

The discussion will be divided into three classes of mine working The first is the open-cut mining of alluvial and detrital deposits, second, dredging of alluvial deposits, and third, lode mining

The principal methods of working open-cut mines are by benches or with inclines, gravel pumps, or by hydraulicking and hydraulic elevators Working by benches is used in mining large, flat, alluvial deposits to 50 to 60 feet deep The mining face is carried in benches Light

80

trestles across the pit provide the shortest possible level distance to the dump The maximum height of the benches is limited, by the dangei of caving, to about 20 feet The overburden is stripped and carried, usually by hand or wheelbarrows, over trestles to the back of the pit The stanniferous earth is carried to the top in baskets to the washing troughs The stacked overburden is kept as close as possible to the working face Drainage of the pit is by gravity when possible or by pumps when necessary All digging is done in the Malay States by a combination pick, mattock, and shovel called a "changkol" Open-cut mines using only hand methods in moving earth geneially advance the faces in a fairly straight line The overburden and tailings from washing are dumped in the woiked-out pit

Inclines are used extensively in the deeper mines up to 200 feet along granite limestone contacts They are often used in other large open cuts to depths of 50 to 60 feet to hoist the waste to the dumps and to elevate the stanniferous earth to the washing plants Pits are worked in various ways They may be advanced in benches, in which case stanniferous earth is loaded in cars on the floor of the pit and trammed by hand to the foot of the incline At times stripping is handled by cars Open pits on contact deposits are usually long and relatively narrow In flat alluvials pit faces are fairly straight, as in bench working Basins or pockets of stanniferous earth, occurring too low in the bottom of the pit for convenient car loading, are worked by being carried in baskets to the washing troughs on the pit floor

Gravel-pump mining usually involves hand work to break the material from the bank, ground sluices to carry the material to a sump, pumps to elevate the materials, and washing troughs for concentration Impounding dams are usually built around the tailings storage area, the water running back into the pit and through ground sluices along the base of the working face Clays and sands are broken down into ground sluices with hoes or bars The face slopes are kept steep enough so that material slides to the sluices by means of gravity The gravel-pump method is applicable over widely varying conditions in different types of deposits It requires a delivery of the entire overburden and the stanniferous earth or "karang" to the sump in the pit floor Working faces are thus continuous from the floor to the surface and assume a roughly circular shape around the sump as a center The entire bank is elevated by the pump and must be stored in the tailings piles at the end of the washing troughs The recovery of over 75 per cent of the tin content in ground sluices is rare Gravel-pump methods provide cheap breaking up of ground, raising of the material at a fairly low

cost, with delivery of the earth to the washing troughs well puddled and with the correct ratio of water for washing

The large percentage of clay and sand and small percentage of coarse gravel, combined with a necessity for puddling of the clay, make Malayan tin deposits far more favorable for successful gravel-pump operation than most gold placer deposits The pumps can handle up to 25 per cent solids, but this pulp is too thick for the washing troughs

FIG 29 —Hydraulic monitors
(Courtesy Malay States Information Agency)

Hydraulicking and hydraulic elevators are used under the same general conditions in tin mining as in the working of gold placers, except that the washing is always done in ground sluices or washing troughs The water is impounded in reservoirs or diverted from streams and conducted in ditches, flumes, and pipes to an elevated point above the deposit, and thence to the working face through pipes A monitor, much like a large fireman's jet, is attached to the end of the pipe by a reducing fitting Monitors in use in a tin mine are shown in Figure 29 A very powerful jet of water issues from the nozzle A three-inch jet under a pressure of 170 pounds per square inch, as is the case at the

Gopeng Consolidated Mines in the Malay States, has a potential energy of about 340 horsepower at the nozzle Such powerful jets break down the toughest deposits with amazing rapidity The most important hydraulic tin mines work alluvial deposits that lie too low for gravity disposal of tailings Hydraulic elevators or large gravel pumps then elevate the material to washing troughs located high enough to allow space for the disposal of tailings Raising the broken ground by the use of hydraulic elevators is still gaining in populaiity in those localities

FIG 30 —Part of the Gopeng Consolidated Company's mine, in 1921
(Courtesy Geological Survey, Federated Malay States)

where sufficient water under natural pressure is available and wheie extensive dumping areas exist at convenient distances from the mine The hydraulic elevator itself consists of a jet of water under a natural pressure of from 60 to 200 pounds, which is caused to shoot out of a nozzle set in a cast-iron frame, up a pipe set parallel to the upward direction of the jet of water The suction resulting from the rapid passage of the water in the pipe is caused to elevate the broken ground by connecting the orifices to a pipe leading from the sump At the Gopeng mine, shown in Figure 30, ground is broken, elevated, and treated by means of hydraulic elevators at a total cost of about 6 cents per cubic yard The method is very wasteful of energy

In general, the large percentage of fine materials in the banks,

absence of coarse boulders, and the necessity for puddling the clayey
materials are much more favorable conditions for hydraulic elevators
than are found in most gold placers Hydraulicking and hydiaulic eleva-
tors in combination have the great advantages of completely puddling
the material, lifting a high percentage of solids, and employing only
small amounts of labor

Simple hand washing devices are important in the industry Pan-
ning has been described The average operator handles 1 25 cubic yards
of sandy material per 8 hours For final concentration, operation of the
pan is the same as for making rough concentrate, but the work is much
slower

Sluice boxes vary widely in different localities The lanchute is
coffin-shaped Material enters near the top, being puddled first if neces-
sary As the sands pass down the box a coolie rakes them with a hoe
The volume of water to that of sand is about 10 to 1, the grade 1 to
16, recovery of tinstone about 90 per cent, and the work of a man per
shift about 12 cubic yards of well-puddled material

Clay puddling is often necessary In small-scale work it is done
with hoes in lanchutes, and in larger-scale work by stage treatment
in small open pits About 60 per cent by volume of water is added to
the stanniferous earth on the pit floor The resultant pulp is scooped
across the floor to the foot of one of the banks, in the face of which is
a series of small basins Coolies at each puddle dip the pulp from one
puddle to the next, and finally to the lanchute on the surface With labor
at 50 cents per day, stage working costs approximately 0 7 cent per
cubic yard per foot lifted In still larger workings, power-diiven drag
machines are used with half-inch discharge screens, the openings of
which are maintained by the use of a water jet The usual method,
however, is by high-speed box puddlers which are similar to log washers
These machines have a large capacity but do imperfect work When
hydraulic elevators oi gravel pumps are used, clay puddling is elim-
inated as these machines do this work effectively

Ground sluices are extensively used in mountainous districts and in
hydraulic mines With a slope of 4 to 8 degrees, their capacity is about
2 cubic yards per hour per foot of width The recovery is often less
than 50 per cent They are cleaned up either by panning the material
in the bottom or by digging it out and concentrating it in a lanchute
The sand in the sluice is allowed to form its own riffles and eddies
No blocks or stops are used

Most of the Malayan tin is recovered in long wooden sluice boxes
called "palongs," such as shown in Figure 31 The typical size is 120

feet long, 4 feet wide, with a 3-degree slope Transverse baffles, usually 10 to 12 feet apart, are used The palongs are either single or in sets of two or more side by side, roofed for protection from the weather, and supported on trestles to give them sufficient height for discharge of tailings Their capacity is about one and one-half cubic yards per hour per foot of width The water feed is about 8 to 1 The material flowing through is stirred manually As heavy sands accumulate, additional

FIG 31 —Sluice boxes or palongs
(Courtesy Malay States Information Agency)

baffles are inserted Clean-ups, usually daily, are effected by streaming down with a small section of clear water The final concentrates carry 15 to 30 per cent cassiterite These are shoveled into buckets and carried to the tin sheds where they are brought up to standard grade in lanchutes It is stated that palongs save about 80 per cent of the tin delivered to them Water-worn cassiterite is easy to recover, but angular grains are difficult to save Lumps of clay cause serious losses Slight overloading causes heavy loss

TIN DREDGING

The first Malayan dredge was started in 1912 Dredging is now the most important method of working alluvial and detrital deposits Dredges allow profitable exploitation of low-grade deposits unworkable by hand The principal factors affecting their design for tin mining are absence of boulders, small size of grains of cassiterite, and large amounts of clay The dredges are of two general classes according to

their method of digging, being bucket dredges and suction cutter type
These are again subdivided as to their method of recovery of the tin-
stone into sluice and classifier-jig varieties Figure 32 shows a tin dredge
in the Malay States dredging 50 feet below water level This particular
unit has a capacity of nearly 4,000 cubic yards per day It is of the
table type with tinstone-saving tables and a tailings elevator Dredges
much smaller in size have been used to a limited extent in Cornwall
Figure 33 shows a small dredge of the bucket type with sluice tables

Dredging for tinstone consists of mechanically breaking up and
elevating low-lying stanniferous deposits and of treating the elevated
deposits by well-known methods The concentrates are retained and

Fig 32 —Tin dredge in the Malay States
(Courtesy Arthur R Brown, Ltd)

the tailings discharged over the end of the dredge The elevated solids
pass into a downward-sloping and revolving steel cylinder or trommel
with a powerful jet of water playing on the solids during their passage
through the trommel Figure 34 shows a dredge trommel being set up
Balls of clay and larger pebbles pass out of the mouth of the screen
The broken solids are forced by the jet of water through the screen
holes into the recovery system

The modern dredges have close-connected buckets ranging from 5
to 12 cubic feet capacity, the latter being about the largest size Ex-
perience in working large properties shows that the economical size is
about 9 cubic feet with an output of 130,000 cubic yards per month
Some of the earlier dredges had open-connected buckets of 10 to 12
cubic feet

The difficulty encountered is not in raising the material but in treating it when raised The tinstone-saving tables required were of such large area that very large pontoons were necessary Recently attention has been turned to jigs Many of the latest dredges are fitted with jigs instead of tables, and it has been found that with skilled attention quite fine tinstone can be saved Generally each jig is driven with its own electric motor, the concentrates from the jigs being taken from the spigots by chutes to a sump From there they are delivered to a "clean-up" jig or jigs The jigs are steel built, with four or eight cells after
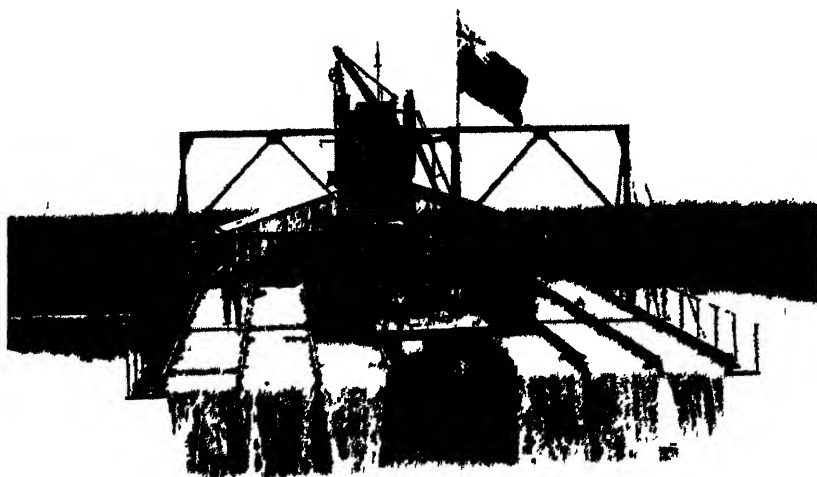
Fig 33 —Small bucket type dredge at work in Cornwall
(Courtesy Werf Conrad, Haarlem, Holland)

the style of the old "Harz" type, but varying in design according to the experience of the different designers

The floating pontoons range from 140 feet to 200 feet long, and from 40 to 60 feet beam They must be built to withstand the enormous stresses encountered The dredging depth ranges from 40 to 60 feet, but dredges are now under construction to dig to 100 feet and over

The spoil raised by the buckets is discharged into a revolving screen supplied with water at a high pressure The stones pass through the screen and are discharged astern by a tail chute or by a tailings conveyor The finer material that passes through the perforations of the screen is led to the tables or jigs for treatment. Steam is generally the

power used, with water tube boilers to burn wood or coal In Malaya the "Rawang" coal is burnt on chain-grate stokers, the boilers also being fitted with superheaters Recently several companies have started to electrify their dredges with a power supply from a central water power station It is not considered economical to build a special generating station for less than four dredges

The water used for washing the material in the screen and tables or jigs is supplied by centrifugal pumps, the quantity varying from 11,000 to 18,000 gallons per minute The jig-saving dredges require less water
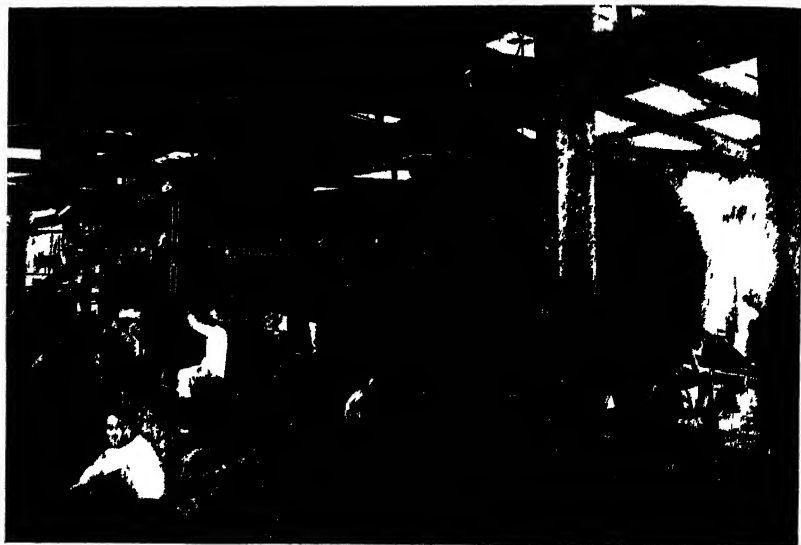
FIG 34 —Tin dredge trommel under erection
(Courtesy Arthur R Brown, Ltd)

The buckets are of cast steel with manganese steel cutting lips The later dredges have manganese steel cast buckets with renewable manganese steel cutting lips, the bucket chain being connected by nickel chrome steel pins The open-connected bucket is generally of the "built up" type with manganese steel pins

The suction cutter dredge differs from the usual bucket type in the manner of elevating the ground A rotating cutter and a powerful gravel pump do the work of the buckets The cutter is ordinarily of the propeller type, being in some cases over 4 feet in diameter It is mounted at the free end of a long flexible steel shaft When the cutter blades rotate under water, they break up the ground against which they are

pressed The broken ground falls into a large orifice connected by a steel pipe to a powerful gravel pump mounted on the dredge proper. A suction dredge operating in the Malay States is shown in Figure 35 For specific details and greater information on dredges, their construction and operation, the reader is referred to Peele's "Mining Engineers' Handbook "

The great advantage of dredging is that low-lying deposits in swampy or very wet ground can be worked at a lower cost per cubic
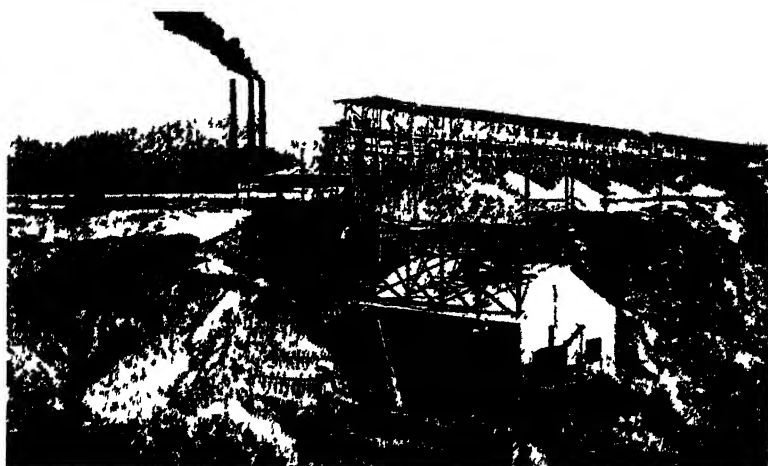
FIG 35 —Suction dredge and elevating gear
(Courtesy Malay States Information Agency)

yard than by any other method Extensive low-grade areas not previously economically workable have been treated with marked success by dredging

Dredging for tin is undoubtedly the cheapest form of mining, provided care is taken that the property is properly prospected and tested and the dredge is designed to suit the property In Malaya the working costs per cubic yard including management expenses run about 8 to 9 cents per cubic yard raised Several have been lower than this where they have had easy ground and good local fuel supplies Many Malayan tin dredging companies have paid 25 per cent dividend for a number of years Ground that contains 1 katti of tin (1⅓ pounds) per cubic yard is considered rich Most companies are paying well on lower values than this Dredging practice has advanced markedly in the last decade It is often prophesied that areas as low in tin content as one quarter pound tinstone per cubic yard will eventually be profitably dredged

LODE MINING

Where the country rock is much decomposed and the tinstone veins are narrow, the ground may be mined by the methods used for detrital and alluvial deposits Pegmatite and quartz veins are usually more 1e-sistant to weathering agencies than most surrounding minerals and rocks Often in tropical climates the country rock can be readily bi oken down by hand labor, whereas the lode itself may require blasting Narrow stanniferous veins may be worked through the weathered zone in this manner

In undecomposed rock, breaking down in the working face is accomplished by drilling and blasting The broken rock is hauled to the surface and to the mill where it is usually crushed in rock bi eakers oi jaw crushers, then pulverized by stamp batteries or grinding mills Often hand picking is practised between the jaw crushers and the stamp battery The ore-dressing flow-sheets which follow give the treatment of various types of ores in considerable detail

ORE DRESSING

Ore-dressing methods of tin-bearing materials will differ widely depending upon their type and source The simplest dressing flow-shee⁻ is shown by those concentrates from Malayan alluvial deposits Bolivian vein deposits are of several different varieties and degrees of complexity Separation of the cassiterite is easy in the simple oxidized oi es where quartz feldspars and iron oxides are the accompanying minerals Concentration of the cassiterite from the complex sulfide oi es is difficult not only because pyrite, chalcopyrite, bornite, arsenopyrite, wolframite, bismuth and silver compounds, galena, and sphalerite are the accompanying minerals, but because the mines are inaccessible and progress is slow Cornwall vein ores are low grade, more or less complex The cassiterite is finely dispersed The ore-dressing methods differ greatly from those in Bolivia Most of the flow-sheets are antiquated The various procedures for ore dressing of tin minerals will be discussed as well as one of the best examples of tailings reworkings

In a typical flow-sheet of a Malay placer tin plant, coarse material is removed on a screen Relatively large amounts of low-grade concentrates are made in sluices This concentrate is often cleaned up by hand on small film sizing tables and hand jigs The gravel or stanniferous earth is excavated by the mining methods previously described (either open-pit mining, hydraulicking, or dredging) On dredges, a revolving stone screen with one-half- to three-quarter-inch holes is ordinarily used

for sizing and disintegrating In hydraulic mining, a sluice grizzly does this work In open-pit mining, the disintegrator resembles a log washer In some cases it consists of a horizontal pan in which the earth and gravel are stirred and raked by rods set in revolving radial arms The oversize from the sizing mechanism goes to waste, the undersize to sluices where separation is made into tailings, containing probably 10 to 15 per cent of the tinstone in the original feed, and concentrate
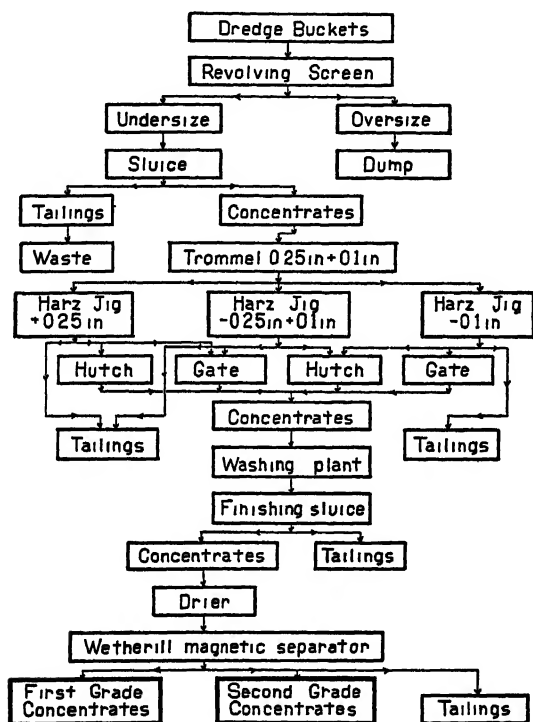

Fig 36 —Flow-sheet of a placer tin dredging plan in Southern Europe (Portuguese American Tin Co)

The sluices or palongs have been previously described under washing devices

The concentrates, depending upon their rate of accumulation, are collected at intervals from several hours to a week The feed of pulp is diverted, the concentrates washed down with clear water and gathered by shoveling Crude concentrates run 10 to 50 per cent cassiterite, the balance being ilmenite, iron ores, pyrite, black sand, and other heavy minerals

The concentrates go to the cleaning sheds for further treatment in lanchute sluices These are 10 to 12 feet long, 9 to 10 inches deep, converging from 3 to 5 feet at the head end to about 15 inches at the discharge end Water is supplied the full width at the head end over a 6- to 7-inch high weir board At first the lanchutes are operated with a fairly strong stream of water while coolies hoe the material, to remove the bulk of the sand tailings These ordinarily run about 0 1 per cent
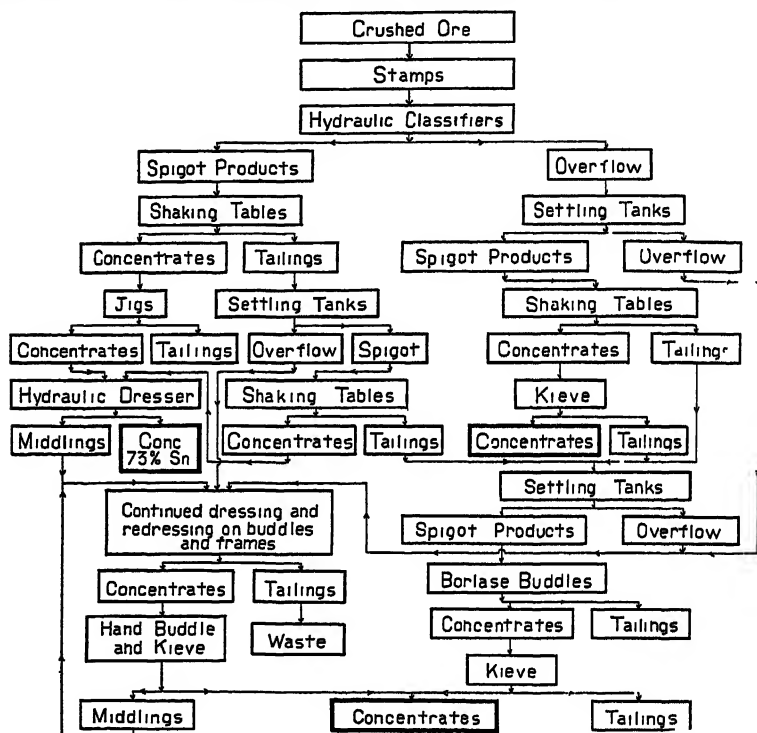
FIG 37 —Flow-sheet of a Tasmanian plant (Anchor Mine)

tin Weak streams of water are then used to collect the coarse portions of the concentrates at one end of the sluice This coarse rough concentrate is jigged by hand in sieves, 12 inches in diameter, 3 inches deep with apertures of 60 to 80 mesh, into concentrates for the market and middlings returned to the sluice for reworking The material remaining in the lanchute after coarse concentrates are removed is further washed with a heavy stream, at the same time being hoed up the slope, giving fine concentrates for the smelter and middlings to be reworked The fine concentrates run 70 to 76 5 per cent tin

Ore dressing of tinstone from alluvial deposits involves no crushing It is essentially two-stage sluicing with hand jigging of coarse-finishing sluice concentrate

In a placer tin dredging plant in Southern Europe, Harz jigs are used in addition to sluices The simplified flow-sheet is given in Figure 36 [1]

Crushed Ore

Ball Mill — Stamps

Drag Classifier

Sand — Overflow

Sectional Trommel — Drag Classifier

+3 mm — -3 mm+15 mm — -15 mm — Sand — Overflow

Harz Jig — Harz Jig — Hydraulic Classifier

Hutch Concentrates — Tailings — Spigot Products — Overflow

Dewatering Cone — Wifley Tables

Spigot — Overflow — Concentrates — Middlings — Tailings

Wifley Tables — Sand Table

Tailings — Middlings — Concentrates

Drag Classifier — Dorr Thickener

Sand — Overflow — Underflow — Overflow

Ball Mill — Tailings — Slime Tables — Waste

Concentrates — Tailings

Alternatives — Dewatering Cone

Oxidized Ore — Sulphide Ore — Underflow — Overflow

Magnetic Plant — Slime Tables — Waste

Shipping — Concentrates — Middlings — Tailings

Fig 38 —Flow-sheet of Avicaya mill

As an example of the treatment of simple low-grade ores, the simplified flow-sheet of a Tasmanian plant working a cassiterite in granite deposit where the mineral is finely disseminated (50% passes 200 mesh) is given in Figure 37 [2] The ore runs 0 10 to 0 16 per cent, the tailings 0 03 per cent, the concentrates 68 to 73 per cent tin The re-

[1] *Eng Mining J*, 104 1109 (1917)
[2] *Mining Sci Press*, 109 65 (1914)

covery is 70 to 75 per cent The ore is exceptionally low grade The ore dressing consists essentially of gravity concentration by repeated roughing of roughly classified products Repeated cleaning of concentrates is practised Middlings are retreated without regrinding

The complex tin ores fall into four general classes The first includes Bolivian sulfide ores low in lead and silver but carrying no other metals of economic value As examples the flow-sheets of the Avicaya mill, Pazna District, Bolivia, and the Llallagua magnetic plant are given The ores of the second class are the same as the first but carry high
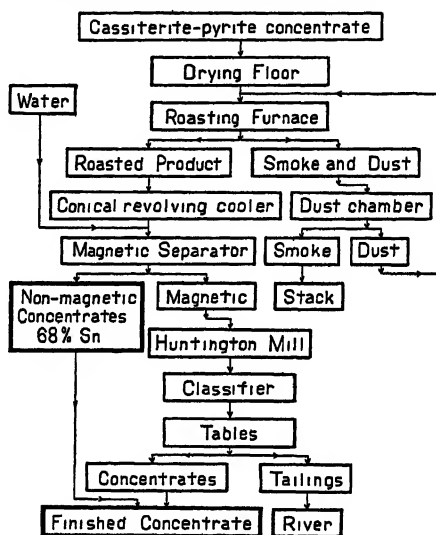
FIG 39 —Flow-sheet of Llallagua magnetic plant

silver values and economic amounts of gold, lead, and copper As an example, the flow-sheet of the Machacamarca, Bolivia mine, Socavon de Oruro is given Cornish ores containing workable quantities of tungsten and arsenic constitute the third class, represented by the flow-sheet of the famous East Pool mine The ores of the fourth class are complex tin, tungsten, and lead minerals, worked for all three metals, as represented by the Butler mine in New South Wales

CLASS I Avicaya mill, Bolivia The ore is partly oxidized, being cassiterite with a siliceous and iron oxide gangue, and partly cassiterite and pyrite in quartz with chalcopyrite, other sulfides, feldspar and tourmaline The average ore runs 5 per cent tin, concentrated to 60 to 65 per cent from the oxidized portions and 50 to 55 per cent from the sulfide parts The tailings run less than 1 per cent tin The flow-

sheet,[3] given in Figure 38, shows fine grinding, step gravity concentration beginning at 3 mm particles Repeated treatments of fine sand are made, giving concentrates for magnetic separation (omitted with the oxidized ore) and middlings for regrinding and further concentration

At the Llallagua magnetic plant [4] (Fig 39), the ore is a cassiterite arsenical pyrite from the gravity concentration mill similar to the one just given above The tin recovery is 93 to 95 per cent with a concentration ratio about 2 to 1 The concentrate, mostly smaller than 1 mm size, is roasted to render it magnetic in a five-hearth furnace, similar to the McDougall, until the sulfur content is lowered from 25 to 27 per cent to 10 to 12 per cent The sulfur oxidation furnishes the necessary heat The roasted concentrate, running 33 3 per cent tin, 12 76 per cent sulfur, 29 3 per cent iron (feed was 31 8% tin, 25 0% sulfur, 24 56% iron), is then cooled, wetted, and magnetically separated into a non-magnetic concentrate running 68 05 per cent tin, and magnetic tailings, which are reground, and then classified into tin concentrate and waste tailings The final concentrates run about 68 67 per cent tin, 4 75 per cent iron, and 3 58 per cent sulfur, with small amounts of nickel, copper, bismuth, lead, zinc, silver, TiO_2, WO_3, lime, and silica The tailings run about 3 per cent tin

CLASS II As an example of the second class of complex ores, the flow-sheet [5] is given in Figure 40 of Socavon de Oruro from which the ore is a complex sulfide and oxide mineral containing tin, silver, gold, lead, copper, iron, antimony, and arsenic in a siliceous gangue The original ore runs 3 to 10 per cent tin with 39 ounces of silver per ton Fine grinding is practised in screen-discharge ball mills in the dry way The sulfide ore is roasted and leached in two stages to recover silver, gold, copper, and lead This is followed by gravity concentration of the leaching-plant tailings In roasting, the sulfur is reduced from 30 to 3 per cent with chloridization (4% sodium chloride) on the last hearth of the three-hearth roasting furnace The concentrates from the jigs and sand tables run better than 60 per cent tin, while those from the slime tables run 30 to 60 per cent and from the buddles [6] less than 30 per cent Round tin-concentrating buddles are illustrated in Figure 41

[3] *Mining Sci Press,* 114 774 (1917), 115 343 (1917)
[4] *Eng Mining J ,* 100 513 (1915)
[5] *Mining Mag ,* 6 301 (1912)
[6] These are stationary washers in which the slope is so gentle that the ore gradually builds up until a bed 10 or 12 inches deep has accumulated The washing is then stopped and the products cleaned out The building up of the sands is regulated by adjusting the tailboards which prevent the ore from rolling off the table They are made convex conical, concave conical, and rectangular

CLASS III The third class of ore is exemplified in the dressing methods of the East Pool mill [7] in Cornwall, given in Figure 42, where a complex mixture is found containing finely disseminated cassiterite along with wolframite, arsenopyrite, and chalcopyrite in a siliceous
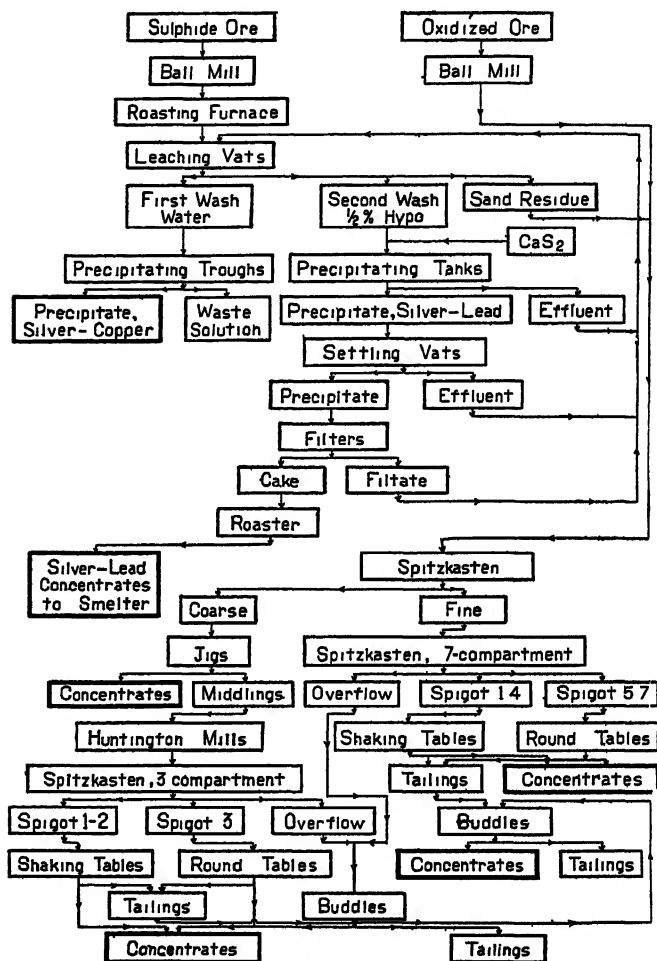
FIG 40 —Flow-sheet of Socavon de Oruro

gangue The ore runs 0 5 to 1 per cent tin, 0 5 to 1 per cent As_2O_3, and 0 25 to 0 5 per cent WO_3 The recovery is about 60 to 70 per cent tin Coarse crushing and gravity stamps are used, followed by gravity concentration to reject rocky tailings The rough concentrates are roasted

to recover arsenic and make iron magnetic This is followed by a leaching treatment to reduce the iron content, and a two-stage magnetic separation to separate tin and tungsten Notwithstanding the usually very fine dissemination of the cassiterite, regrinding of tailings is not practised As a result, practically no tin not freed in the primary grinding is saved

CLASS IV The fourth class of complex tin ores may be exemplified by the flow-sheet [8] of the Butler mine in New South Wales, given in Figure 43, where a complex tin-tungsten-lead ore is worked The recovery is about 8 per cent of tin, 68 per cent WO_8, and 64 5 per cent

FIG 41 —Round buddles for tin concentration in Bolivia

of the lead Jaw crushers and gravity stamps break up the original material, followed by collective gravity concentration on tables, vanners, and frames This is coupled with flotation of gravity concentrate to separate the lead Tin and tungsten are separated magnetically from the flotation tailing

As an example of modern practice for the recovery of tin from tailings running only 0 6 per cent tin, the flow-sheet [9] of the Treskillard Minerals in Cornwall is given in Figure 44 The large tonnage of tailing stacked by the old Grenville, West Frances, South Frances, and West Basset mines, in Cornwall, is now being profitably treated A recovery of about 75 per cent is obtained, or over 9 pounds of tin concentrate (54% metal) per long ton of material treated From 50

[8] *Eng Mining J ,* 106 530 (1918)
[9] *Eng Mining J ,* 124 773 (1927)

Run of Mine Ore

Crushers

Stamps

Hydraulic Classifiers

Spigot Products | Overflow | Rectangular Frames

Wilfley Tables | Concentrates | Tailings

Tailings | Middlings | Concentrates | Round Tables

Frue Vanners | Concentrates | Middlings | Tailings

Tailings | Concentrates | Acme Tables

Settlers | Frue Vanners | Concentrates | Tailings

Sand | Slime | Tailings | Concentrates | Rectangular Frames

Copper Concentrate | Roasting Furnace | Concentrates | Tailings

Wilfley Tables | As_2O_3 | Round Tables

Tailings | Concentrates | Concentrates | Tailings

Kieves | Roasting Furnace

Thickened Solid | Overflow | Round Table | As_2O_3

Drier | Mill Circuit | Concentrates | Tailings

Tube Mills | Round Table

Hydraulic Classifiers | Concentrates | Tailings

Spigot Products | Overflow | Wetherill Magnetic Separator

Wilfley Table | Round Table | Partially Magnetic Sn-Fe | Magnetic Sn Fe-W | Non Magnetic Sn

Tailings | Concentrates | Tailings

Automatic Sampler | Leaching Tank 1% Sulphuric Acid

Reject | Sample | Residue | Effluent

Waste | Drier | Waste

Wetherill Magnetic Separator

Magnetic Concentrates (Wolframite) | Non-magnetic Concentrates Sn

Kieves | Kieves

Concentrates | Mill Circuit | Concentrates

FIG 42 —Flow-sheet of the East Pool mill

```
                        Crushed  Ore
                           Stamps
                     Hydraulic Classifiers

   Spigot 1      Spigot 2        Spigot 3      Overflow
                   Wilfley Table              Callow Tanks

   Concentrates   Middlings        Sigot      Settling Box

 Hydraulic Cleaner   Kieve      Wilfley Tables  Spigot  Overflow

   Concentrates   Middlings    Concentrates  Middlings  Tailings

            Kieve                      Vanners

      Middlings    Concentrates              Tailings


                           V-Box

               Overflow      Sand

               Rectangular Frame

               Concentrates   Tailings

               High-speed Vanner

               Concentrates   Tailings

   Classifier                    Dewatering Box

   Sand    Overflow    Spigot Waste      Overflow

  Berdan Pan                 Slime Tank

  Flotation Machine    Spigot Waste    Overflow

 Lead  Concentrates    Tailings      Mill  Supply Tank

                       Dryer

                  Magnetic Separator

               Magnetic      Non-magnetic
              Concentrates   Concentrates
              (Wolframite)        Sn
```

FIG 43 —Flow-sheet of the Butler mine

to 60 long tons of mixed sand and slime per day are handled by the plant No novel tin-concentrating appliances are used The apparently crude appliances used for the concentration of tin ores are susceptible of fine adjustment and delicate work Efficient concentration and mini-mum loss of metal are obtained by separate treatment of products of varying degrees of grade and of coarseness All products alike in grade and size of particles, irrespective of origin, must be treated together

TIN

Stress is laid on the importance of classification In general, a machine that is delicately adjusted for one class of product will not treat any other class efficiently

Thorough classification begins immediately after the primary grinding by tube mills The discharge goes through a series of classifiers
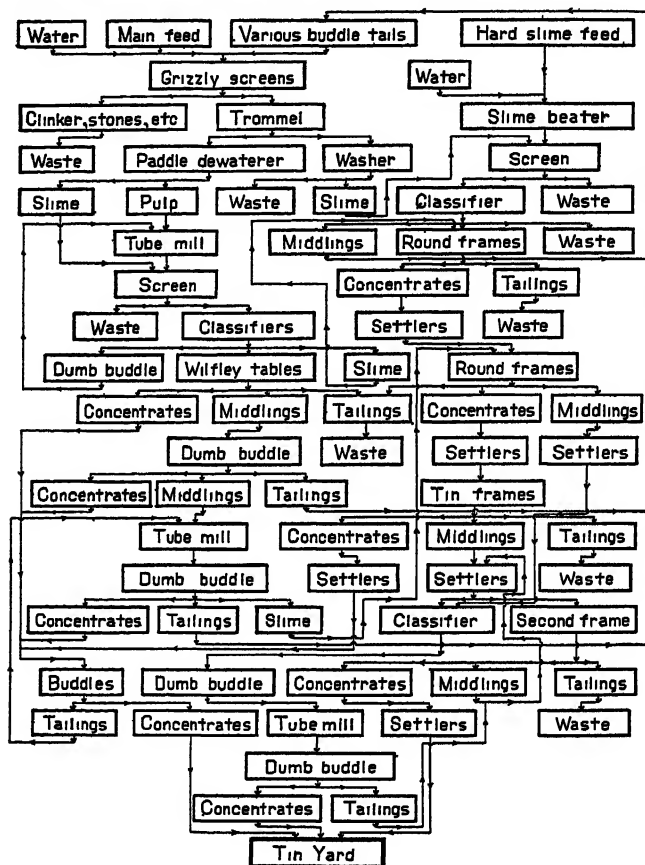
FIG 44 —Flow-sheet of the Treskillard Minerals in Cornwall

and then to Wilfley tables where each pair of tables treats only material supplied by its own classifier These tables make a head which goes for final treatment to the tin yard, where the heads from each pair of tables are buddled separately Before being reground, the Wilfley middlings are buddled This buddling yields a small amount of high-grade head and a small tailing, suitable for return to the primary grinding circuit

The secondary fine grinding of tailings in this flow-sheet is particularly to be noted as well as the very efficient use of the buddle It is stated that total treatment costs are about 16 cents per long ton of ore treated It is obvious that this type of plant requires highly skilled operation and close supervision

SPECIAL TREATMENT OF ORES

It is often necessary to treat specially the tin concentrates from some localities so as to remove objectionable metallic impurities, with the object of making them more suitable for smelting and the production of a purer final metal Concentrates from vein deposits such as Bolivian may require extensive preparation before smelting Concentrates from alluvial sources require relatively little pre-treatment

There are a number of general methods which may be broadly classified into (1) roasting followed by further mechanical separation of minerals which have been physically broken away from the cassiterite as the result of the process or altered in such a manner, e g , as change in specific gravity, making them more amenable to further mechanical concentration, (2) roasting under controlled conditions followed by leaching with water or acid solutions, (3) heating with sodium salts such as soda ash, sodium chloride, salt cake, etc, followed by leaching, (4) metallic impurity removal by oil flotation when the impurities are present as sulfides These will be discussed rather briefly

When calcined at a red heat, cassiterite is unchanged but many of the associated minerals of metals other than tin are altered Much of the sulfur and arsenic and some of the antimony are volatilized The volatile products, particularly arsenious oxide, are sometimes collected either in bag houses, Cottrell installations, or other dust-collecting equipment The roasted concentrates contain tin oxide, oxides of iron, zinc, bismuth and copper, lead sulfate, small quantities of more or less unaltered sulfides, tungsten compounds, and minor amounts of other minerals

Roasting is done in furnaces of many types, either of a hand-rabbled reverberatory variety or in multi-hearth mechanical furnaces Hallett[10] states that perhaps the most popular furnaces are those of the rotating cylinder type, as the Oxland and Hocking, and the White-Howell These are made with a heavy steel or cast iron cylindrical shell 30 to 40 feet long and 4 to 6 feet in diameter, lined with firebrick In appearance, they are somewhat similar to cement kilns Coal or oil is used as fuel, the burners being located at the discharge end The fixed-hearth

[10] Liddell, "Handbook of Non-Ferrous Metallurgy," New York, 1926, McGraw Hill Book Company, Inc , Vol 2, p 1376

revolving-rabble type furnaces such as the Wedge, Heireshoff, Mac-
Dougall, Ridge, Pearce turret, Merton, and related kinds are also
used Multiple hearths are usually employed, the top hearth being
sometimes used as a drier The furnace capacities are about a ton of
tin concentrates per hour with a fuel consumption of 100 to 300 pounds
of coal per ton of concentrates The material to be roasted is usually
crushed to pass a quarter-inch screen Roasting temperatures are from
550° to 650° C

Roasting is often followed by leaching with water or acid solutions
to remove the products made soluble by the roasting process

Tungsten-bearing tin concentrates are usually heated with sodium
carbonate or sodium sulfate at 600° C, to form sodium tungstate
Excess sodium salt is avoided, otherwise some of the cassiterite will be
converted to sodium stannate The sodium tungstate is soluble in water
and is leached from the treated concentrates, recovered from the leached
liquors by evaporation, and purified for the market Although this
method has been used in a number of localities, it has not been very
satisfactory Hand picking of tungsten materials is the method now
generally used to remove them from the concentrates before smelting

When the concentrates carry considerable quantities of sulfides, a
chloridizing roast, followed by leaching, is sometimes used This method
is often employed on Bolivian silver-tin ores and silver-tin-lead con-
centrates When the sulfides are roasted with salt (NaCl) in an oxi-
dizing atmosphere, sodium sulfate and the chlorides of the metals are
formed with no attack on the tin oxide Many of the chlorides are
fairly volatile Bismuth, lead, arsenic, antimony, and silver may be thus
partially removed in the form of fume The chloridizing roast is usually
followed by suitable leaching and washing in wooden vats, in some
cases fitted with filter bottoms The furnaces for the chloridizing roast
are similar to those used for dead roasting with the exception that
1 to 5 per cent of salt (NaCl) is mixed with the concentrates before
they are charged into the furnace

Most common metal sulfides are easily separated from oxide ores
by oil flotation While this method has not been extensively used in pre-
paring tin ores or concentrates for smelting, it is known that the process
may be applied and may assume considerable importance in the future

SALE OF CONCENTRATES

The purchasing of tin concentrates by the smelters is chiefly done
by contract, usually on an annual basis, calling for delivery of a cer-
tain definite tonnage, although some of the smelters make a definite

practice of buying small parcels whenever offered for sale Usually 96 to 98 per cent of the tin content of the concentrates is accounted for, depending on the kind of ore The concentrates must run ordinarily at least 60 per cent tin Bolivian tin concentrates, or "barilla," usually contain 58 to 70 per cent tin, while those from the alluvial deposits, especially the Straits, contain 70 to 76 per cent tin, the balance being slag-forming constituents The tin in Straits concentrates is easily reduced with the production of a resultant metal of high purity, while the treatment of the Bolivian concentrates is extremely complicated

The procedure involved in calculating the amount of the payment for the ores differs somewhat with the different individual smelters In some cases payment for all the tin is made, the smelting losses and other factors being taken care of in the treatment charge The value of the tin is usually determined by taking the average of the prices ruling on the London Metal Exchange for "spot" and "three months standard" tin as quoted during the second calendar month after the shipment is made This means that if a shipment be made on January 14th, the liquidation would be made as per the average of the quotations for the month of March

The returning charge and final settlement for the ore is made in pounds sterling The rate of exchange in recent years has been an important factor in governing the net returning charge Therefore, to offset fluctuations in the rate of exchange and to stabilize the returning charge, the value of the pound sterling may be fixed for the duration of the contract All transactions are based on a ton of 2,240 pounds

The concentrates are nearly all purchased on a 60 per cent tin basis For each unit (1%, or 20 pounds per short ton, 22 4 pounds per long ton) or fraction thereof above or below 60 per cent, the returning charge is reduced or increased at the rate of five shillings per unit The net returning charge has varied from £10 to £25 ($48 to $120) The basic price for standard tin is generally taken at £170 ($816) per ton, and the returning charge is increased or decreased at a fixed rate for each pound sterling, the settlement quotation is above or below £170 One per cent of sulfur is allowed free and is penalized at the rate of ten shillings per unit or fraction thereof over 1 per cent

Five per cent of iron is allowed free and is penalized at the rate of ten shillings per unit or fraction thereof over 5 per cent The usual splitting limits on assays are as follows tin 0 5 per cent, sulfur 0 2 per cent, iron 0 2 per cent

The undesirable constituents, such as lead, copper, arsenic, antimony,

and bismuth, are not penalized specifically, but an increased treatment charge is made to cover costs occasioned

On tin concentrates, the determination of the settlement assay is always made by the fire-assay method, *i e ,* fusion with sodium cyanide The method is unreliable at its best As most metals are reduced by the cyanide, their removal is necessary before fusion Many are removed by prolonged treatment of the finely divided sample with hydrochloric acid and nitric acid Iron is difficult to eliminate entirely, and, if present as magnetite, it is never completely removed Tungsten and silver are removed, if present, by treating the residue with ammonium hydroxide

Lang [11] states "Small amounts of tin are retained in the slag Silica causes incomplete recovery of tin Up to 10 per cent SiO_2 the error is not large, but above this it soon becomes prohibitive These errors, together with absorption and volatilization, are usually less than the error due to the iron and other impurities reduced with tin in the button Correction for purity of the button is not allowed The cyanide-tin results are always checked by a reliable wet method "

A number of American tin metallurgists feel that the cyanide method is not a bad one if the purity of the tin button be determined This is always done in the plants in the United States

[11] "Marketing of Metals and Minerals," New York, McGraw Hill Book Company, Inc, 1925

CHAPTER 6

SMELTING AND METALLURGY

The only American book on tin metallurgy in the last twenty-five years is that of Henry Louis—"Metallurgy of Tin" In his preface in 1911, Louis says

This little work is in the main a reprint of a monograph on the metallurgy of tin, published originally in MINERAL INDUSTRY for 1896, Vol V Authentic information on the subject of tin smelting is somewhat scarce, and as the above-mentioned volume has long been out of print, it was decided to issue the monograph as a separate work, incorporating in it as much recent information on the subject as was obtainable The small amount of new matter is due to two reasons first, the unprogressive character of tin smelting, which continues from decade to decade with comparatively little change, and, secondly, the profound degree of secrecy observed by tin smelters, who are extremely anxious to keep to themselves any modifications or improvements in processes These two facts, the slow advance of the industry and the secretive habits of those engaged in it, are related as effect and cause

Until the World War period, the chief improvements in practice originated in the Pulo Brani Works of the Straits Trading Co at Singapore, Straits Settlements, Federated Malay States These works produce 30,000 to 50,000 tons per year There is no doubt that they constitute one of the main reasons why tin metallurgy has not kept pace in any measure with that of other common metals Tin is by far the rarest Comparing the world's annual output of the common metals —copper 1,900,000 tons, lead 1,820,000 tons, zinc 1,560,000 tons, aluminum 230,000 tons, and tin 175,000 tons—the marked difference is sufficiently striking It must be remembered that several individual copper, lead, and zinc plants produce more than 100,000 tons a year, close to the total annual tin production When metallurgical operations are conducted on a small scale, they are more likely to be surrounded with secrecy In consequence, improvements come slowly, and ancient methods survive with surprising tenacity

REDUCTION OF TIN OXIDE

Practically the only source of primary tin is the stannic oxide ore, cassiterite The winning of tin from its ores consists essentially of causing the conversion of the stannic oxide, SnO_2, to elemental tin

This can be accomplished in a variety of ways, only one of which is now in commercial use and of present economic importance

Stannic oxide can be reduced by carbon at fairly high temperatures Cassiterite can be reduced to tin metal by certain reducing gases, such as hydrogen and carbon monoxide, commercial gases containing these or mixtures of them, or at a lessened rate by hydrocarbons and gasified oils

The possible metallurgy of tin divides itself naturally into several subdivisions by following through the analogy of other non-ferrous metals

A Reduction and removal of oxygen by carbon and related solid reducing agents

B Reduction and removal of oxygen by gaseous reducing agents

C Leaching of the ore (as in the case of copper) with direct separation of the metal from the leaching liquors

D Converting stannic oxide to a soluble form and decomposing the compounds formed

E Solution and decomposition in a fused salt bath (as the Hall process for aluminum)

F Electrolytic reduction at the cathode in aqueous solutions

G Reduction of cassiterite by metals

H Combinations of the above methods or combinations of parts of the above methods

The only commercial method today is the first in the classification, that of reduction by solid carbonaceous material The second, that of gaseous reduction, is, because of its manifold advantages, a method of the future

The reduction of tin from its oxide is not difficult Reduction takes place readily at fairly high temperatures in the presence of reducing agents such as coal, culm, or coke The required temperature for smelting is determined principally by the composition of the slags which are formed The smelting temperature must be sufficiently high to keep the slags fluid, and allow the reduced tin metal to settle and collect in the bottom of the furnace

Inasmuch as the smelter has only one ore to deal with, the metallurgy of tin is comparatively simple Its reduction in practice is almost invariably accomplished by the aid of carbonaceous materials Several complications occur, however (1) The temperature of reduction is so high that the oxides of other metals, present in a greater or lesser degree, are reduced at the same time These metals may produce undesirable and troublesome tin alloys The iron-tin alloy, "hardhead," is

an example (2) Tin oxide is amphoteric Unless conditions are carefully regulated, the furnace linings are attacked Siliceous acid linings cause tin silicates to be formed, basic linings of lime or magnesia result in losses as stannates The great difficulty in tin smelting is caused by the fact that tin oxide readily combines with silica to form tin silicates During the smelting of the concentrates mixed with flux and fuel, a considerable amount of tin invariably combines with silica and goes into the slag in the form of readily fusible tin silicates mixed with other more or less complex silicates which make up the slag On the other hand, if an extremely basic slag be used, tin oxide will act as an acid and enter the slag The slag components must be nicely adjusted It is desired to produce slags of as low a tin content as possible, as the principal loss in tin smelting is in the tin carried off by the slags The making of low-tin slags is, however, not of the greatest importance in the primary smelting of tin concentrates (3) Tin metal at elevated temperatures is more fluid than is mercury at ordinary temperatures It finds the most minute openings for escape and soaks into the porous refractories of furnaces to an amazing degree (4) The slags produced contain appreciable quantities of tin This metal must be recovered Slags require further treatment also, there may even be treatment of successive slags for their tin content Part of the tin in the slags is present mechanically retained as "prills," or small metallic globules Unduly large amounts of metal go into the slag, which may run 10 to 25 per cent tin

There are therefore three stages in the smelting of tin ores or concentrates (1) Reduction, or tin smelting proper, (2) cleaning the slags and furnace linings and recovery of tin from them, (3) refining the impure tin

TIN-SMELTING FURNACES

Smelting furnaces used for tin are of two types,—the blast or shaft furnace, being set vertically, and the reverberatory furnace, being set horizontally The blast furnace is much older, being in most general use in the early industrial life of tin smelting Treatment in reverberatories did not come into use until well along in the eighteenth century Full development of the reverberatory method did not occur until about the middle of the nineteenth century

In its simplest form, the blast furnace consists of a short vertical shaft, circular, square, or rectangular in cross section, and of moderate height Charcoal is used as a fuel in alternate layers between the layers

of concentrates Air is supplied by a blast, almost invariably cold, through tuyeres, located a little way from the bottom of the furnace

Pryce[1] states that the reverberatory furnace was introduced into Cornwall for tin smelting with fossil fuel in the beginning of Queen Anne's reign (about 1705), but up to that time the shaft furnace, or "blowing house" as it was called, with charcoal as a fuel, was always used Primitive furnaces still exist and are operated in the far East, even as crude as the pre-Roman method of digging a hole in the ground and throwing tinstone on a charcoal fire excited by a bellows

Pryce[2] also states that "The Cornish tin-miner took his cleaned stream tin to the blowing house, paying the owner of the house twenty shillings for every tide or twelve hours, for which the blower was obliged to deliver to the Tinner, at the ensuing coinage, one hundred pounds gross weight of white Tin for every three feet or one hundred and eighty pounds of Stream Tin so blown, which is equal to fourteen pounds of Metal for twenty of Mineral, clear of all expense "

He describes the smelting process as follows

The furnace itself for blowing the Tin is called the Castle on account of its strength, being of massive stones cramped together with Iron to endure the united force of fire and air This fire is made with charcoal excited by two large bellows, which are worked by a water-wheel, the same as at the iron forges They are about eight feet long and two and a half wide at the broadest part The fire-place, or castle, is about six feet perpendicular, two feet wide in the top part each way, and about fourteen inches in the bottom, all made of moorstone (*i e*, granite) and clay, well cemented and cramped together The pipe or nose of each bellows is fixed ten inches high from the bottom of the castle, in a large piece of wrought Iron, called the Hearth-Eye The Tin and charcoal are laid in the castle, stratum super stratum, in such quantities as are thought proper, so that from eight to twelve hundredweight of tin, by the consumption of eighteen to twenty-four sixty-gallon packs of charcoal, may be melted in a tide or twelve hours' time Those bellows are not only useful for igniting the charcoal, but they throw a steady and powerful air into the castle, which, at the same time that it smelts the Tin, forces it out also through a hole at the bottom of the castle, about four inches high and one and one-half inches wide, into a moorstone trough six and one-half feet high and one foot wide, called the float, whence it is ladled into lesser troughs or moulds each of which contains about three hundred pounds of Metal, called Slabs, Blocks, or Pieces of Tin, in which size and form it is sold in every market in Europe, and on account of its superior quality is known by the name of Grain Tin, which brought a price formerly of seven shillings, that is further advanced, the last two or three years, to ten or twelve shillings per hundred more than Mine Tin is sold for, because it is smelted from a pure Mineral by a charcoal fire, whereas Mine Tin is usually corrupted with some portion of Mundick [pyrite], and other Minerals, and is always smelted with a bituminous fire, which communicates a harsh, sulphureous, injurious quality to the Metal

In the Far East, particularly in China, fairly pure cassiterite is smelted in very crude small blast furnaces No definite slag practice, except a rule of thumb one, is followed The tin metal produced is

[1]"Mineralogia Cornubiensis," p 282 (1778)
[2]*Loc cit*, p 136

usually of poor grade Many of the furnaces consist of bamboo cylindrical forms, lined with clay

When tin ores from Cornwall became a factor in England, shaft furnaces were built of stone and brick and operated with positive-pressure blowers for the draft Figure 45 shows an old Cornish "tin castle," reproduced from the 1832 edition of Karsten's "System of Metallurgy"

Modern steel-shell, brick-lined blast furnaces, with water cooling, are used all over the world for tin smelting Practice in operation is similar to that employed for other metals, although tin shaft furnaces

Plan

Vertical Section   Front Elevation
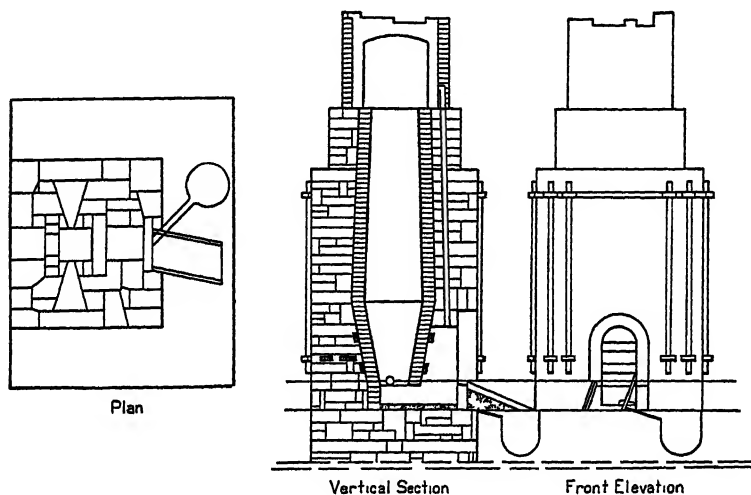
Fig 45—An old Cornish 'tin castle"

are built with somewhat lower shafts, to operate with comparatively low blast pressures Coke is the usual fuel Brick "settlers" or fore-hearths are sometimes used to collect liquid slag and tin metal as they are tapped from the furnace The slag usually overflows from the settler to the slag pots These are removed and the molten slag poured into water to granulate it, or it may be allowed to freeze and then be broken up mechanically

Metallic tin is tapped from the bottom of the settler at intervals and run off into cast-iron molds The tin pigs ordinarily need refining, usually done by thermal methods

Reverberatory smelting of tin concentrates dates back to the early part of the eighteenth century, when reverberatory furnaces were introduced into Cornwall They have increased in favor for they are

adaptable not only for primary smelting but also for slag treatment
to recover tin Reverberatory furnaces produce somewhat cleaner slags
in the primary smelting, as well as in the resmelting of first-run slags
The operations are more readily controlled in reverberatories than in
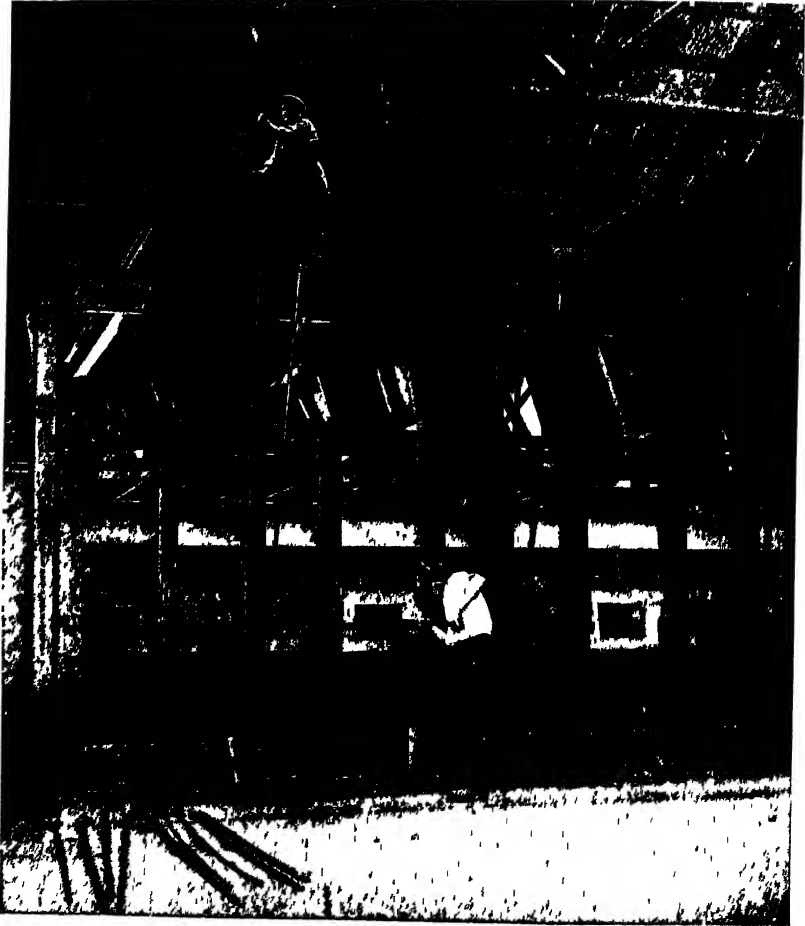
Fig 46—Tin smelting reverberatories at Penpoll
(Courtesy The Mining Magazine, London)

blast furnaces The reverberatory is particularly suited to the smelting
of fine tin ores and concentrates because of the lower dust losses The
furnaces are constructed of firebrick and vary greatly in size Hearths
on the largest ones are approximately 30 feet long and 12 feet wide

The fire box is at one end and the flue and stack connection at the other Figure 46 shows one of the most modern tin reverberatories, one of those at the Penpoll smelter at Bootle, England The fuel is long-flame bituminous coal, although oil is sometimes used Eight- to twelve-ton charges are typical for the larger furnaces The usual charge consists of tin concentrates with 15 to 20 per cent of anthracite screenings,

Fig 47—The Lodge electrostatic dust collector for flue gas at Penpoll
(Courtesy The Mining Magazine, London)

small amounts of slag-making materials such as sand and limestone, old slag and refinery by-products Premixing of the charge constituents is usually accomplished outside the furnace The process is entirely a batch operation The smelting time of the larger furnaces is usually 10 to 12 hours, at temperatures of 1200° to 1300° C, ordinarily Relatively large amounts of tin are allowed to go into the slag, as such practice tends toward the production of metal containing a minimum amount of impurities After the batch is smelted, practice in handling

the fluid slags and tin is the same as in blast furnace operations Reverberatory furnace slags usually run 10 to 25 per cent tin Rabbling in the furnace is accomplished with iron hoes attached to long iron handles which are operated through the side doors of the furnace The stirring is usually done as completely as possible

Tin-smelting reverberatory furnaces are constructed of firebrick, having a hearth sloping toward the tap hole which is usually placed at about the center of one side of the furnace and low enough to drain the furnace completely The roofs are of arch construction, of the same type as that generally employed in metallurgical works for this kind of smelting unit Charging is done through several holes in the roof Some type of dust-collecting equipment is usually found on the flue end of a smelting system A modern dust collector, as shown in Figure 47, is often of the electrostatic precipitation type

TREATMENT OF SLAGS

Slag produced in the first-run smelting of tin concentrates invariably contains so much tin that it must be retreated before being discarded Retreatment is done in furnaces of either the blast or the reverberatory type Second-run slag from blast furnaces generally contains higher tin percentages than those from slag-smelting reverberatories The object in slag smelting is to reduce the tin silicates to metallic tin Higher temperatures are required than are used for concentrates smelting Fairly large amounts of reducing materials are required, being added as culm or anthracite screenings Limestone may be employed as a fluxing material and often metallic iron in the form of scrap is used to replace the tin in the silicates in the slag Tin produced from slag smelting is usually very impure, generally containing considerable amounts of iron-tin alloys These are known as hardhead In the best practice, secondary slags should not contain more than 1 per cent of tin, although often slags containing 3 per cent or more are discarded Some of the richer slags at times are added to the concentrates charge in the first smelting

Sixteen to eighteen hours is the time for reverberatory slag smelting The operation is a batch process Handling of liquid slags and the metallic tin resulting is the same as in blast furnace practice

REFINING OF TIN

The metallic tin produced from smelting is too impure to be sent to the market as such Refining to eliminate objectionable metallic impurities alloyed with the tin is of two kinds. the thermal method,

which will be described here, and the electrolytic method which, because of its future possible importance, is described in a separate chapter

The thermal refining consists of one or both of the operations of liquating or sweating and boiling, tossing, or poling Liquating is done in a comparatively small sloping-hearth reverberatory furnace with the hearth slope toward an open tap hole which discharges into receiving kettles outside the furnace Liquation has for its object the removal of those metallic impurities, alloys and compounds having a higher melting point than tin The bars, pigs, or slabs of tin are placed on the upper side of the furnace hearth The furnace temperature is kept just above 232° C, the melting point of tin Long-flame bituminous coal is used for fuel The melting is slow The success of the operation depends on careful temperature regulation to avoid melting the metallic impurities The tin runs from the furnace to the outside kettles, leaving the residue on the hearth The dross remaining in the furnace is pushed toward the fire and the temperature is raised until all possible metal is recovered The second sweated portion of tin is caught in another kettle, cast into pigs or slabs and resweated with the next charge The final dross is treated at a higher temperature and roasted, the resultant product going to the tin concentrates smelting furnace

Some impurities of comparatively low melting points are sweated out with the first-run tin metal Most of the iron, arsenic, antimony, and copper impurities remain with the dross, while most of the lead and bismuth go into the tin

The first-sweat tin is further refined by boiling or tossing This is done in kettles holding 6 to 10 tons at temperatures considerably above the melting point The boiling operation is analogous to copper poling, inasmuch as the molten metal is stirred with a pole of green wood or by immersing in it bundles of green wood sticks The wood undergoes destructive distillation, the resultant steam and gases producing a strong bubbling or boiling action in the bath Thus different portions of the metal are brought to the surface and exposed to the air Most of the impurities and part of the tin are oxidized The drosses collecting on the surface are skimmed off, to be either resweated or else resmelted with an original tin concentrate charge In some of the more modern refineries, boiling is done by agitating the metal with compressed air Boiling is continued until the desired grade of refined metal is produced If the tin contain large amounts of impurities, the operation may be continued for several hours Excessive heating at too high a

temperature must be avoided, otherwise large amounts of tin will be oxidized

Tossing consists in filling hand ladles with the molten tin and pouring it from a height back into the kettle, thus exposing it to the oxi-
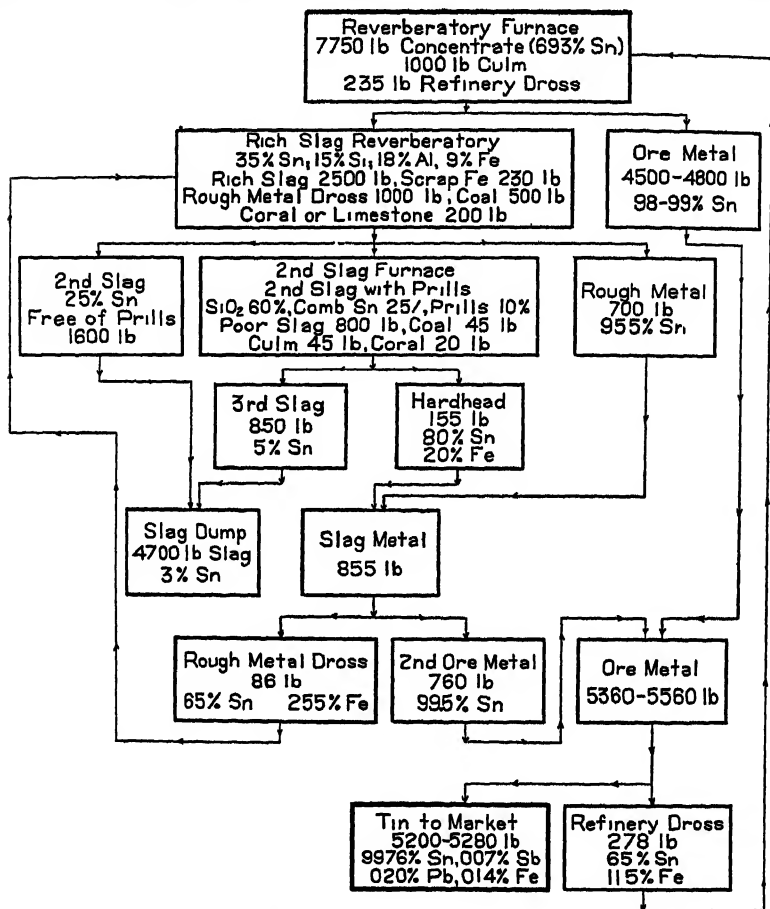
FIG 48—Flow-sheet of the Pulo Bram Works of the Straits Trading Co

dizing action of the air The result is quite the same as that of boiling

Iron is almost completely removed by boiling, while the other impurities such as arsenic and antimony are considerably reduced in amount

After refining, tin is cast into pigs The dross is carefully skimmed off in the kettle before casting so that the metal will have a clean, bright

surface Tin is cast at temperatures just slightly above its melting point, in cast-iron molds quickly filled and lightly skimmed with wooden paddles just before solidification of the metal

One of the most eminent smelters in the world is the Pulo Biani Works of the Straits Trading Company This plant is on an island off Singapore, Straits Settlements A process and tonnage flow-sheet of the operations is given in Figure 48 Reverberatory smelting furnaces are used, a special feature of the furnace being the water vault The lower part of the furnace foundation, below the ground line, is built so as to form a water tank the full length of the hearth and the length of the holding kettle An eight-foot depth of water is maintained Any tin leaking through the furnace bed or through joints drops into the water and is thus granulated, this material being collected periodically As it is absolutely impossible to prevent leakage of so mobile and easily fusible a metal as tin, this water vault presents to the smelters a satisfactory method of handling leakage and recovering the metal

Straits practice is summed up in the following operations Alluvial concentrates are smelted with carbonaceous material to produce "ore metal" and "rich slag" high in tin The rich slag is smelted with the aid of coal and scrap iron to produce "rough metal" and "poor slag " The "poor slag" is smelted for prills, producing "hardhead" and another low-grade slag which is sent to the dump "Hardhead" and the rough metal, together making the "slag metal," are refined, the dross returning for reprocessing, the refined slag metal joining the "ore metal " The total metal recovered from the concentrates is refined by liquation, poling, or tossing It is stated that in continuous operation 97 to 98 per cent of the metal present in the original concentrates is recovered The iron consumption amounts to about 5 per cent of the tin produced, and the coal consumption 25 to 30 per cent Concentrates run from 65 to 70 per cent or better in tin They are of alluvial or "stream" origin, thus being very pure

Cornish practice is shown in the second flow-sheet (Fig 49) It differs from Straits practice in that ordinarily iron as raw material is not used to replace tin in the slags as a method of recovery The slags are subdivided to a greater extent and a greater number of varieties of tin are produced Cornish smelters have to use Bolivian vein ores, diluted with alluvial concentrates Furnace liquation is used in Cornwall more often in the treatment of the impure tin metal produced Concentrates are mixed with 15 to 20 per cent of culm, a small amount of lime as a flux, and often some slags, drosses, or other tin-bearing

products from other stages of operations The materials are mixed and dampened before charging into the furnace Furnace temperatures are of the order of 1200° to 1300° C After rabbling and settling, about

FIG 49 —Flow-sheet of Cornish smelting practice

two-thirds (the upper two-thirds) of the slag is withdrawn and sent to the dump Another portion is reworked by stamping and crushing for prills The slag tailings go to the dump, the prills being reworked

with the remainder of the slag, which contains appreciable tin in the combined form

Tin metal from reverberatory smelting is cast into molds, the "glass" slag with it being removed and sent to the slag furnace The cast tin is liquated, the hardhead going to the slag furnace for reworking The liquated tin is "boiled" by poling with billets of green wood or admitting air under pressure, and the heavy impurities are allowed to settle out The top layers of the boiled tin are cast into molds, and, depending upon the purity of the metal, sold as refined tin or as block tin Drosses return to the concentrate smelting furnace for reworking, the lower layers from the boiling kettle are mixed with the

FIG 50 —The Anglo-Oriental smelter, Penpoll, at Bootle, England
(Courtesy The Mining Magazine, London)

metal recovered from the slags and other products The slags containing appreciable tin, the prills, hardhead, and glass slags are treated with some culm in the slag reverberatory The resultant slags, running from 2 to 5 per cent of tin, are discarded Metal tappings from the furnaces are cast into molds and liquated, the liquid is boiled, and the top layers are cast into molds and sent to the market as common tin The bottom layers are returned to the slag reverberatory, along with the drosses, for reworking, and the hardhead produced from liquation is either discarded or smelted with antimony or lead ores to produce antimony, tin, or lead-tin alloys which can be disposed of as such

The most modern and recently completed British smelter, that at Penpoll, is shown in Figure 50 The plant was "blown in" during the latter part of 1928 The Penpoll smelter is located almost within a stone's throw of another of the world's large tin smelting plants, that of the Williams, Harvey & Co , Ltd , which was recently partially rebuilt and modernized

AMERICAN TIN-SMELTING PRACTICE

Refining tin by furnace methods is at best an imperfect operation, for large quantities of impurities cannot be separated The quality of the metal produced depends very largely on the original purity of the concentrates American tin-smelting practice, when plants existed in the United States for the treatment of foreign tin ores, was more advanced than any others so far developed In 1903, R T White, in Bayonne, N J , built a plant for the International Tin Co to smelt Straits of Malacca (Malayan) concentrates The British government then placed a 40 per cent ad valorem export duty on tin ores to other than British smelters, so the plant failed, owing to lack of raw material at a price which would allow the enterprise to continue In 1915, tin shortages in the United States and the availability of Bolivian vein ores again made possible the establishment of tin smelters

The flow-sheet of the Maurer plant of the American Smelting & Refining Co is given in Figure 51 This plant treated Bolivian ores exclusively The material termed "ore" is a concentrate containing between 55 and 65 per cent of tin, with arsenic, antimony, iron, copper, tungsten, bismuth, lead, and sulfur as impurities The ore was given a preliminary roast in a Wedge furnace to drive off sulfur by oxidation and antimony and arsenic by volatilization The ore from the Wedge furnace was mixed with blast-furnace dust (recovered in the bag house) in a mechanical mixer It passed on to a Dwight & Lloyd sintering machine, where it was sintered with lime and sometimes silica Lime was added to the sinter charge to protect the grate bars of the machine and also for fluxing the sulfur remaining in the ore The sintered ore passed to the blast furnace, where it met drosses from various operations, coke, and the fluxes or slag-forming materials

Special care had to be taken in proportioning the slag so as not to get it too basic, under which condition the tin compounds in the ore formed stannates and were lost in the slag, and not too acid, under which condition tin silicates formed were similarly lost

The best proportions of the slag components were found to be 38 to 40 per cent silica, 22 to 28 per cent iron oxide (FeO), and 38 to 40 per cent lime, magnesia, and alumina An average slag in good tin-smelting practice was about 33 per cent silica, 28 per cent iron oxide, and 28 per cent lime Finished slags were of about the following percentage composition SiO_2, 35 , FeO, 18 , CaO, 28 , Sn, 2 8 to 2 5 , and the remainder, MgO and Al_2O_3

Very good slags, metallurgically speaking, were 3 4 sesquisilicates
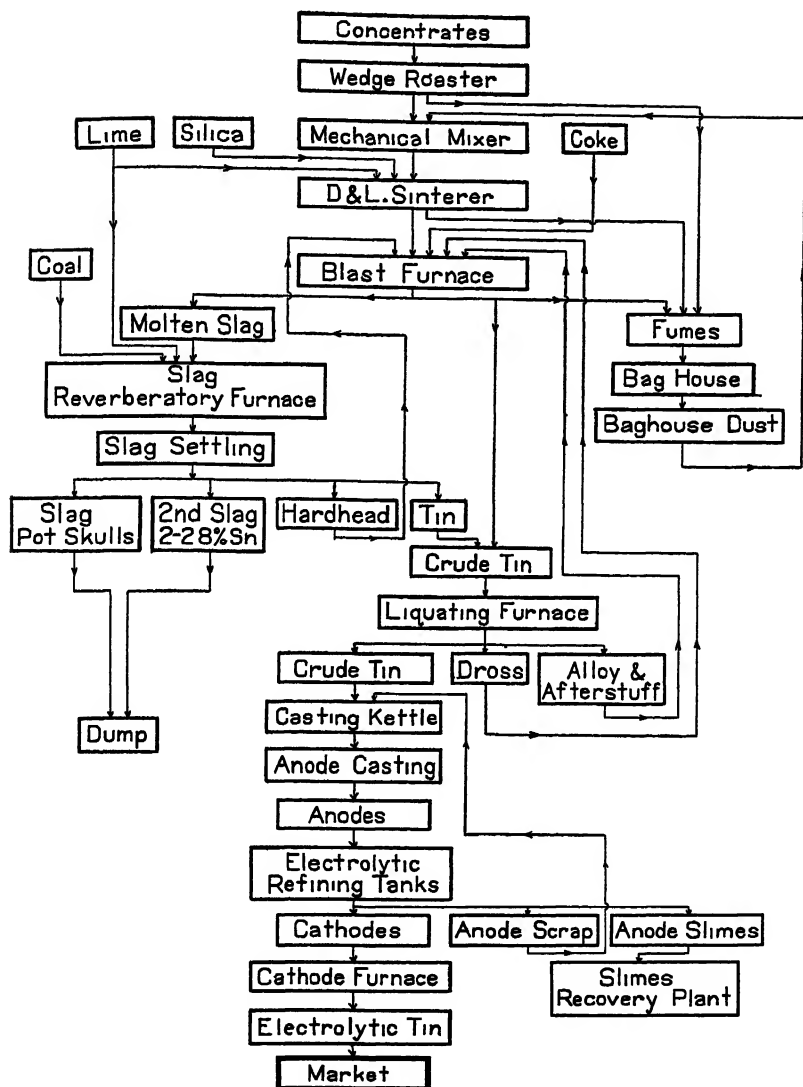
FIG 51 —Flow-sheet of American practice

In the blast furnace the stannous oxide, when produced, acted as a basic constituent, whereas the stannic oxide acted as an acid one It is interesting to note at this point that the stannous sulfide was volatile at 1075° C, whereas the temperature of the blast might go as high as 1400° C.

In practically all plants the first slag produced from the blast furnace contains such large quantities of tin that it must be retreated practically as if it were an original ore At the Maurer (New Jersey) plant it was claimed, however, that better than 90 per cent of the tin in the original ore was recovered and that there was little volatilization of tin compounds

In the Maurer flow-sheet, the blast furnace produced a crude tin, which went to the liquating furnace, and a high tin slag running 6 to 10 per cent tin, which was sent in the molten condition to the slag reverberatory Fumes from the blast furnace were collected in the bag house, returning to the process by mixing and sintering with fresh ore The slag, at 1100° C, was raised to about 1300° in the slag reverberatory and treated with lime and coal It was then settled Tin metal produced was either sent to the liquating furnace, joining the tin from the blast furnace, or placed in the casting kettle for casting into anodes The slag from the reverberatory, containing 2 0 to 2 8 per cent tin, was sent to the dump Slag-pot skulls went to waste Iron-tin alloy or hardhead was returned to the blast furnace

The crude tin from the blast furnace was liquated and then cast into anodes on a continuous anode-casting wheel Dross, alloy, and scrap returned to the blast furnace The anodes were sent to the electrolytic refinery and refined in a manner almost identical with that for copper, using lead-lined tanks and a sulfate-fluosilicate electrolyte The product, ready for market, was 99 8 per cent tin

The anode slime, which, in the refining, in contradistinction to copper refining, clings to the anodes, was washed from the anode scrap and worked up for bismuth, and in some cases for arsenic, antimony, lead, and other constituents Anode scrap was returned to the anode furnace for recasting into anodes

Electrolytic tin is lower in impurities than any of the foreign brands of tin It is claimed that an average of three-fourths of a ton of slag was produced per ton of 60 per cent concentrates smelted The tin loss in slags was 1 5 to 2 5 per cent of the tin Electrolytic refining losses were 10 pounds per ton of 97 per cent tin anodes refined Tin recoveries were of the order of 94 to 97 per cent of the metal originally charged as concentrates

At present, all the American smelters are closed, as English smelters can satisfy American requirements at a lower cost English smelters offer to treat tin concentrates for £10 or even less per long ton

CHAPTER 7

GASEOUS REDUCTION, LEACHING, AND METALLIC REDUCTION

A review of the smelting of tin warrants the conclusion that present practice is not as simple as might be expected from the mere chemistry of eliminating oxygen from an oxide of a common metal It is not always appreciated that nearly all of the difficulties in present-day tin-smelting operations are due to the rebellious nature of highly heated tin metal Furthermore, the actual reduction mechanism is not as direct as the generally assumed equation $SnO_2 + 2C = Sn + 2CO$ would lead one to believe The old Chinese reduction process, employing solid carbon, has been known and employed in various forms for thousands of years

Leplay and Laurent in 1837 [1] ingeniously showed that solid carbon reduction is gaseous in its mechanism and that physical contact of reducing agent and reducible oxide is not essential They placed a piece of solid carbon in a platinum boat in a furnace tube sealed at one end, in another boat alongside of the first they placed metallic oxides Stannic oxide was used in some of the experiments The tube was heated in a furnace, the open end in contact with the air The solid carbon oxidized to carbon monoxide and dioxide and the metallic oxides were reduced to metal without contact with the solid reducing agent

The work of Fink and Mantell [2] on stannic oxide and finely ground tin concentrates has confirmed these results They calcined stannic oxide at 850° for one hour in the presence of air The tin concentrates were roasted at 850° to 1000° C for four hours Graphite, ball-mill ground, was calcined at 850° for one-half hour and at 1000° for two hours in closed crucibles in the absence of air Determinations were also made in which calcined fuel coke and calcined petroleum coke were used

Stannic oxide was placed in an alundum combustion boat This boat was placed alongside a similar one filled with ground graphite Both boats were placed in the center of a vitreosil tube 24 inches long, of 1-inch diameter The tube was heated in an electric furnace. Purified air was drawn through the heated tube Determinations were made

[1] *Ann chim phys* (2) 65 404 (1837)
[2] *Eng Mining J*, 124 686-691 (1927)

at 600°, 700°, 800°, and 900° C each No reduction was evident at 600° and 700°, reduction at 800° was very slight, but it was easily seen at 900°, with the production of small tin globules on the surface of unreduced stannic oxide Substitution of tin concentrates for the stannic oxide gave similar results Further runs were made with stannic oxide and fuel coke, concentrates and fuel coke, stannic oxide and petroleum coke, and concentrates and petroleum coke Practically all of the results were the same Reduction was determined by testing the charges, after the run was over, by qualitative chemical methods The furnace charges were cooled in nitrogen (freed of moisture, oxygen, and carbon dioxide) to room temperature before being examined

Doeltz and Graumann [3] report that carbon reduction of stannic oxide was not evident after one hour at 800° C, but did show signs of taking place at 830° to 900° It is interesting to observe that carbon slowly oxidizes at 500°, the oxidation of amorphous carbon is marked at 650°, and the speed of oxidation increases upon further rise of temperature Commercial blast and shaft furnaces used for tin smelting operate over a range of from about 1000° to 1400° C

Charpy and Bonnerot [4] attempted to determine whether reduction of iron oxide (Fe_2O_3) by carbon may be brought about by direct action between the solids or through mediation of the gas phase only They studied the rates of reduction under a series of low pressures Ferric oxide and graphite, previously purified, heated to 1000° in vacuum, mixed and strongly compressed, were heated in an electric furnace in a porcelain tube The pressures were maintained and measured by a mercury pump and MacLeod gage At 950° C, under pressures of 0 01, 0 1, 1, 2, 4, and 8 mm of mercury, the following rates of evolution of gas were found 0 10, 0 14, 0 31, 0 56 0 80, 1 07 cc per hour The rate thus rapidly decreases with decrease of pressure and the conclusion is drawn that, at least up to 950°, solid carbon does not reduce ferric oxide If solid carbon does not reduce ferric oxide (when the carbon cannot oxidize owing to the absence of oxygen in the surrounding atmosphere) up to 950°, it will not reduce stannic oxide, which it will be shown later is harder to reduce than is ferric oxide

Fink and Mantell [5] confirmed this finding in respect to stannic oxide Finely ground graphite and stannic oxide were calcined at 850° for one hour These were intimately mixed and compressed in a small hand-press to a more or less compact mass Ten-gram charges were placed in alundum boats in a tube furnace in a nitrogen atmosphere

[3] *Metallurgie*, 4 290 (1907)
[4] *Compt rend*, 15 644(1843)
[5] *Loc cit*

and subjected to temperatures of 600°, 700°, 750°, 800°, and 850° for four-hour periods The charges were cooled to room temperature before being removed from the furnace and its nitrogen atmosphere The nitrogen had been purified of oxygen After cooling, the charges were tested qualitatively by sensitive methods for tin The reduced metal was absent in all cases

These experiments were repeated with finely ground (ball mill), acid-washed fuel coke and finely ground petroleum coke treated with concentrated sulfuric acid These carbonaceous materials were previously calcined to remove volatile matter These materials were intimately mixed with calcined stannic oxide and treated as were the materials used in the experiments previously described In no case was tin found by qualitative tests

Carbonaceous fuels in air atmospheres, out of contact with stannic oxide or tin concentrates, have the power of reducing tin oxides by their own oxidation and passage to the gaseous phase Carbonaceous fuels intimately mixed with stannic oxide, in the absence of oxygen, are without reducing properties, at least up to 900° C Solid carbon fuel reduction of reducible metallic oxides is gaseous in its mechanism Carbon reduction requires higher temperatures than gaseous reduction, as the carbon must first be gasified at a rapid rate This rate becomes marked above 1000° C

In ordinary smelting operations, the coal or coke of a reducing charge is active only as it becomes partly oxidized to carbon monoxide gas Reduction of metallic oxides is not accomplished by reducing fuels in the solid phase If a more efficient, cheaper, and more easily manipulated process would result from the gasification of the reductant, outside of the smelting furnace, the possibility of developing such a process deserves careful consideration The gaseous reduction of tin concentrates has been studied with this end in view

Tin in metallic form has a low melting point It is different from most of the other metals occurring in the combined state in nature, in that its ore has a reducing temperature, by gaseous reductants, above the metal melting point

Present reverberatory and blast-furnace practice in the metallurgy of tin requires temperatures of 1300° to 1400° C Hydrogen reduction may be effected beginning at 250° C, and the most economic point is between 750° and 800° C The choice of hydrogen is suggested by the location of the world's largest tin orebodies, such as those of Bolivia, in regions far from coal but in the midst of sources of water power "Smelting with water" seems to be the obvious answer to the problem

Gaseous reduction was first investigated in 1830 by C Despretz,[6] who reported that hydrogen and carbon monoxide each reduces stannic oxide to tin metal W Muller[7] reported his work on heated oxides in contact with hydrogen in sealed glass vessels He showed that many metallic oxides give evidence of reduction at temperatures from 200° to 400° C

A E Arnold[8] and W Hampe[9] propose hydrogen reduction of tin ores for one or two hours on a 1-gram sample at a red heat as an analytical test They point out the advantage of the ease of separation of the reducible oxides of the metals from those non-reducible (those of silica, non-metallic minerals, gangue) by acid treatment of the reduced charge and resulting metal solution

Fink and Mantell[10] studied the reduction of stannic oxide by specially purified hydrogen between the temperatures of 250° and 1000° C Determination of the rate of change of velocity of the reaction

$$SnO_2 + 2H_2 = Sn + 2H_2O$$

with change of temperature was made No data exists in the literature The method of determination was to subject charges of pure tin oxide to a stream of hydrogen gas which had been carefully purified in an electric furnace with temperature control They found that stannic oxide could be completely reduced by hydrogen to metallic tin at temperatures as low as 250° C The reaction was caused to proceed as an irreversible one, by inducing an excess of the reactant, molecular hydrogen, to act as a medium of removal of the undesired product of the reaction, water vapor, by causing the gas to sweep across the reacting surface

With stannic oxide in excess of the amount required to oxidize all of the hydrogen present to water vapor, at any particular temperature, further reduction ceases as soon as the water vapor concentration has attained N per cent, where N is a function of the temperature The value of N varies inversely as the temperature The hydrogen gas must be supplied at a sufficiently high rate to maintain an excess of reductant for the stannic oxide, and at a velocity high enough to "sweep out" water vapor as fast as it is formed

There must be sufficient excess of reductant to prevent the reoxidation of the reduced products of the reaction As the reaction is between a solid material and a gas, the natural inference is that the reduction resulting is a surface phenomenon Stannic oxide is reduced in two

[6] *Ann chim phys* (2), **43** 222 (1830)
[7] *Pogg Ann*, **136** 51 (1864), **153** 332 (1875)
[8] *Chem News* **36** 238 (1877)
[9] *Chem Z* **11** 19 (1887)
[10] *Eng Mining J*, **127** 967 972, 1052 1054 (1927)

steps or in one step, depending upon whether the temperature employed is below or above the thermal decomposition point of the lower or stannous oxide

The velocity of the reduction was not the same for all parts of the mass and continued greatest at those points first affected This same phenomenon has been observed by Hilpert [11] in his work on the reduction of iron oxide by hydrogen and carbon monoxide The curve for the results given in Figure 52 covers the temperature range of 250°
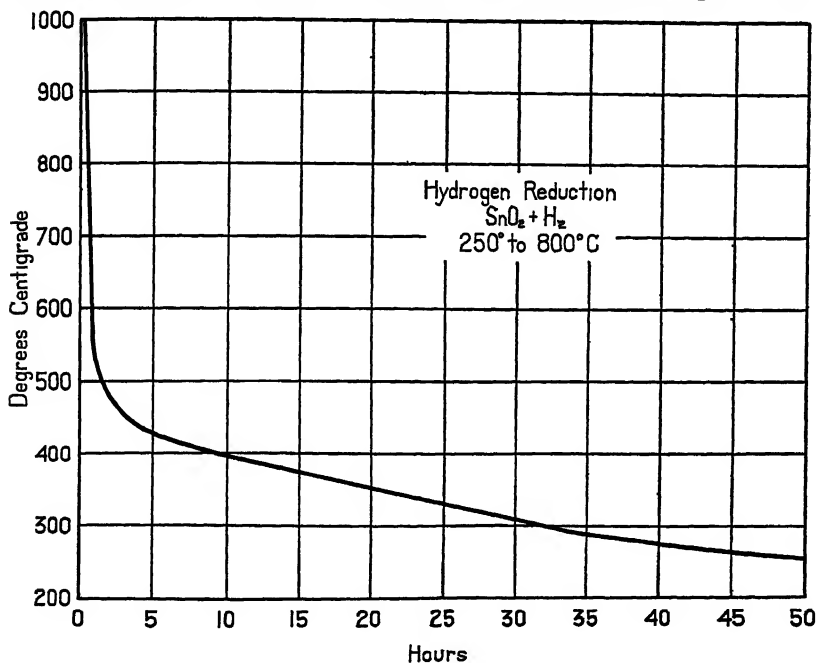
Fig 52 —Relative reduction rates of stannic oxide at various temperatures

to 850° C The curve for the reduction is logarithmic The general expression was found to be $\log T_k + \log M = C,$ where T_k is the absolute temperature, M the time, C a constant Extrapolation of the curve shows that the reaction would be instantaneous at 1000° C , and would require many days at 100° C , assuming reaction possible at that temperature

The shape of the curve shows that the most advantageous temperatures at which to operate are those above 750° C , when rapidity of reduction is desired When the curve for stannic oxide is plotted with

[11] *Ber,* 42 4574 81 (1909)

a relatively small time interval as ordinate, the curve can be seen to have a distinct inflection at approximately 750° C

Fink and Mantell [12] determined the rate of reduction of ferric oxide in comparison with stannic oxide, in order to gain an insight into what happens in a complex ore containing iron and tin oxides together, as well as the oxides of the other metals Pure ferric oxide was used

The time-temperature curve for the reduction of ferric oxide by hydrogen is given in Figure 53 As was the case with stannic oxide, the velocity of the reduction was not the same for all parts of the mass, being lessened and continuing greatest at those points first affected For ferric oxide the curve is shifted over closer to the axes than is the stannic oxide curve

The conclusion is drawn that ferric oxide reduction by hydrogen is easier than stannic oxide reduction by hydrogen In a mixture of these oxides the tendency would be first, for a reduction of the ferric oxide, second, a stage where both were being reduced, the ferric oxide at a faster rate than the stannic oxide, and, third, a stage where all the ferric oxide was reduced with some stannic remaining

Reduction of tin oxide by hydrogen is rapid at 700° to 800° C The commercial possibilities of this method are many Temperatures necessary are far below those used in tin smelters today Future possibilities are indicated by the large-scale investigations now under way Results, based on experiments over a wide range of temperatures, indicate practical commercial operations at from 750° to 900° C In practically all of the previous work on gaseous reduction of tin ores, it has been observed that metallic iron did not appear as such after reduction and cooling of the charge The oxides of iron were always evident From the fact that metallic tin was always found, and no metallic iron, it was concluded by earlier investigators that the oxide of tin was more readily reduced to metal than were the oxides of iron This reasoning has been shown to be unsound Fink and Mantell [13] studied this from the viewpoint of the oxidation of hydrogen-reduced tin and iron They found no difficulty in producing hydrogen-reduced iron either from any of the iron oxides or from those oxides mixed with the oxides of tin, provided the charges are cooled to room temperature after reduction in a reducing atmosphere A quantity of hydrogen-reduced iron was made and its oxidation studied Some samples of commercial hydrogen-reduced iron as well as finely ground electrolytic iron were procured The oxidation points of these materials were studied All three of the

[12] *Eng Mining J* , **127** 967 972 (1927)
[13] *Eng Mining J* , **124** 1052 1054 (1927)

varieties of iron mentioned showed rapid oxidation by moist air at 200° C

The hydrogen-reduced iron oxidized more rapidly than did the electrolytic iron after contact with the stream of air for 30 minutes The hydrogen-reduced iron was pyrophoric at this temperature All three forms of iron showed definite oxidation at 150° C and at 100° C At 75° C the electrolytic iron showed relatively little oxidation, but the hydrogen-reduced product showed an appreciable amount At 50° C
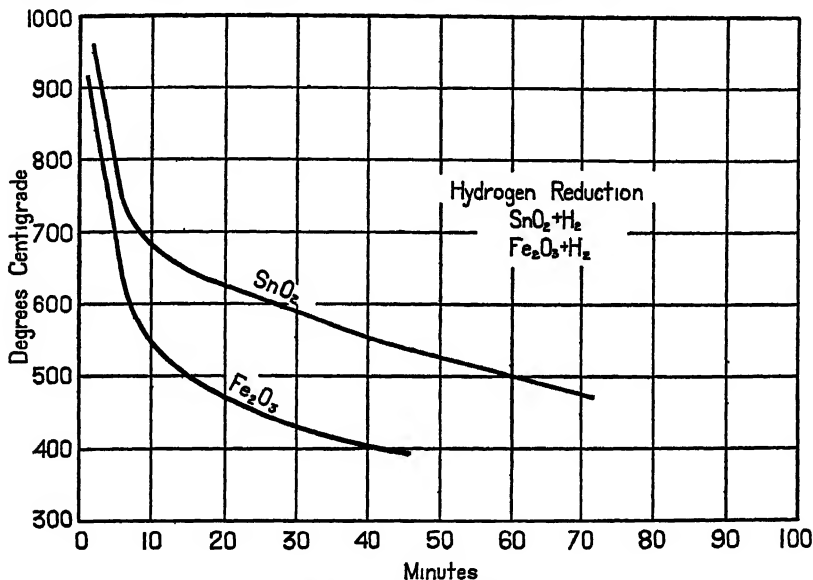
Fig 53 —Curve showing time necessary for complete reduction of stannic oxide and ferric oxide at various temperatures

only the hydrogen-reduced iron made in the laboratory showed oxidation, and the commercial material did not

The same experiments were repeated using dry air Results were quite similar and in the same sequence, with the exception that the finely divided hydrogen-reduced iron was pyrophoric as low as 150° C

Apparatus was arranged so as to allow reduction of ferric oxide to iron by hydrogen, then allowing the introduction of nitrogen to sweep out the hydrogen, and then allowing a stream of air to be introduced Boat loads of freshly reduced iron were found to be pyrophoric and completely oxidized at 200°, 150°, 100°, 75°, and 50° C , and in one case even at 40° C

Hydrogen-reduced iron, prepared at temperatures far below its
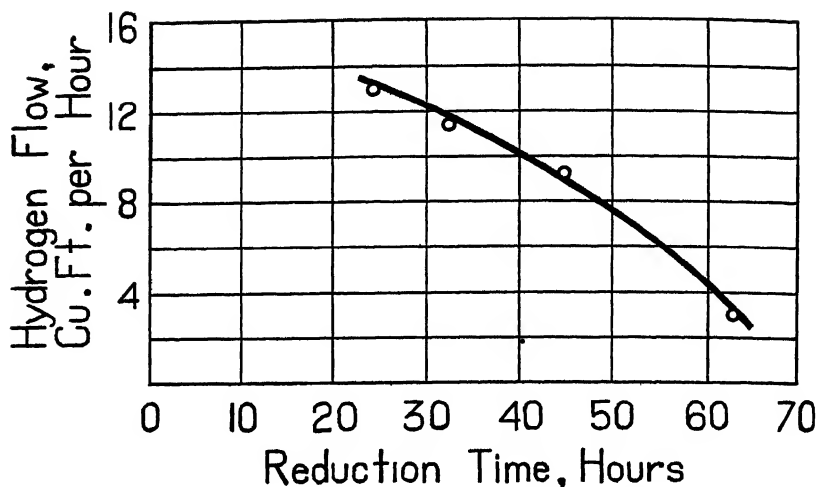
FIG 54 —Curve showing flow of hydrogen and time of reduction at constant
temperature

melting point, is in the form of a very fine powder The average particle
size will be of the order of 2 to 3 μ The surface of these particles in
comparison with their volume is enormous Their ready oxidation at low
temperatures is thus easily understood from what we know of surface
absorption phenomena

Metallic tin, when the reduction temperature is 200° or more above
its melting point, tends to form small drops or globules, thus reducing
the exposed surface Experiments were made with tin particles reduced
at low temperatures to determine their temperature of oxidation The
experimental procedure was the same as outlined above The tin par-
ticles were of the order of 2 to 3μ There was little oxidation of tin at
50°, 75°, 100°, and 150° C either by moist or by dry air over a half-
hour period At 200° C there was a slight oxidation, which grew less
after passing beyond 230° to 250° C , when there was a tendency
toward the formation of globules At no temperature below 250° C
nor at 250° C was the tin pyrophoric

We thus have the explanation for the absence of iron in the ex-
periments of other workers in the reduced masses resulting from the
reduction of mixed iron-tin oxides or of iron-bearing tin concentrates
Knowing that tin was not oxidized to any appreciable extent below its
melting point, the furnaces used were usually discharged after cooling
down to or a little below the melting point of tin The reduced iron,
being freshly prepared and very active, is readily reoxidized at these
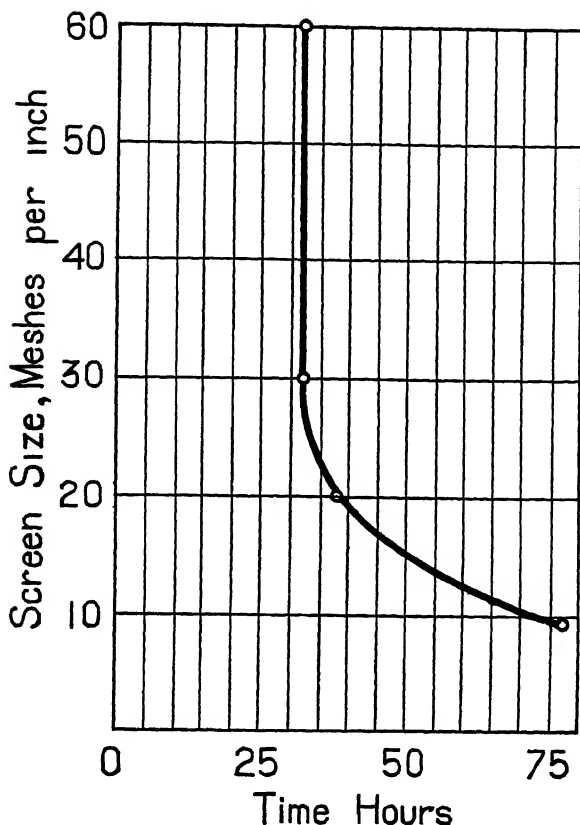
FIG. 55 —Curve showing screen size and time of reduction

temperatures—so readily oxidized that it is pyrophoric On contact of
the reduced masses with the air, the reduced tin metal is not affected,
but the reduced iron changes over entirely to its oxides

Hydrogen reduction of Bolivian tin concentrates on a semi-com-
mercial scale shows time-temperature reduction curves of the same form
as the tin-oxide-hydrogen curves At any temperature the time for
complete reduction was a function of the hydrogen flow velocity as
shown in Figure 54 Time of reduction varied with the mesh of the
ore up to 30 mesh, as shown in Figure 55 Beyond this screen size
further grinding of the ore did not seem to increase the speed of con-
tact between ore particle and gas molecule

The process of gaseous reduction depends for its success upon the
absence of all slagging phenomena until complete reduction is effected
Even incipient fusion prevents the intimate or rapid contact of ore and

gas, slowing down the reduction finally to complete stoppage, when the ore particles become slagged or glazed over In the particular Bolivian concentrates used, no difficulty was encountered due to the low fusing point of tourmalines, gangue materials, or slagging ore constituents at the temperatures employed After reduction the furnace charge was cooled in an atmosphere of hydrogen to below the melting point of tin Iron was always found as oxides in the reduced charge, the cause of which has been explained above

In its final solution, the method of tin recovery from the reduced charge was simple The concentrates had the following analysis SnO_2, 86 2 per cent, Sn, 67 95 per cent, Fe, 4 19 per cent, Fe_2O_3, 5 65 per cent, Sb, 0 04 per cent, As, 0 010 per cent, Cu, 0 036 per cent, Bi, 0 296 per cent, WO_3, 1 42 per cent, SiO_2, 1 73 per cent, and S, 0 28 per cent If the ore charges were stirred or rabbled continuously during reduction, thus exposing fresh surfaces and allowing the molten tin particles to flow together, about 80 per cent of the tin content of the ore was directly liquated from a non-fluid slag

This metal was about 70 per cent of the weight of the concentrates charged into the furnace The remaining 20 per cent of the tin content of the concentrates could be almost completely recovered by fusing the residues at 1000° to 1050° C when the gangue formed a very liquid slag and the metallic tin readily settled out The slag contained only small amounts of tin amounting to 1 to 2 per cent of the total tin content of the original concentrates

The final slags were from 10 to 12 per cent of the original weight of the ore The tin contained all the reducible metals, bismuth, antimony, lead, copper, and silver, but only a small amount of the iron Arsenic was absent in the tin produced, and had evidently been volatilized in the process Tungsten and molybdenum were reduced to their lower oxides only, and did not find their way into the metal

Investigation shows also that there may be possibilities of winning tin from its ores by low-temperature gaseous reduction (300° to 500° C) followed by leaching of the reduced charges, with electrolytic precipitation of the metal in the leaching liquors The leaching solutions, after partial removal of their metal content, can be used again for leaching of fresh reduced ore Almost 100 per cent metal extraction is possible The possibilities have as yet been little explored

Using hydrogen for the reduction of tin concentrate, a rough estimate of the power consumption is based on the following factors One pound of metallic tin requires for its reduction from cassiterite (SnO_2), 6 cubic feet of hydrogen gas One kilowatt-hour produces 7 cubic feet

of hydrogen gas by the electrolysis of water [14] The theoretical value is about 9 cubic feet Power requirements for the production of hydrogen therefore are 0 86 kilowatt-hour per pound of metallic tin, or 1,030 kilowatt-hours per ton of 60 per cent tin concentrate The reaction is effected economically at 750° C At this temperature the power requirements for heating represent an additional 1 75 kilowatt-hours per pound of tin, or 900 kilowatt-hours per ton of 60 per cent concentrate The total power requirements then appear as 1 6 kilowatt-hours per pound of tin, or 1,930 kilowatt-hours per ton of 60 per cent concentrate

Smelting costs employing carbonaceous fuel for reduction are about $48 per ton of 65 per cent concentrate [15] About 41 per cent of this cost is for fuel,[16] or $19 68 per ton of 65 per cent concentrate The same operation by gaseous reduction, with power at $0 003 per kilowatt-hour, will amount to $5 97 per ton of concentrate Even if power were as expensive as $0 01 per kilowatt-hour, the total cost of energy for reduction by hydrogen would be $19 30 per ton of concentrate Gaseous reduction would not have to carry the 1 per cent of the smelting cost for fluxes that carbon reduction entails, and the 15 per cent for general expense (a portion of which is for refractories) would most likely be materially reduced

Leaching of Tin Concentrates and Tin Oxides

This work was undertaken to find some single substance or combination of substances which, in aqueous solution, would dissolve stannic oxide If it be possible to dissolve native stannic oxide with some solvent or combination of solvents, the foundation will then be laid for a leaching process for extraction of tin from its ores or, in other words, the hydrometallurgy of tin It was also hoped that the work might throw some light on the mechanism of the secondary enrichment of tin ores F W Clark [17] states that the solubility of cassiterite is indicated by several natural deposits Cassiterite has been noted in opaline deposits, from hot springs, as pseudomorphs after feldspar, cappings on quartz crystals, and in stalactitic forms

A hydrometallurgical process for recovering tin analogous to those processes used on copper by the Chile Copper Company at Chuquicamata, or the New Cornelia Copper Company at Ajo, Arizona, would profoundly affect the tin industry The leachable copper ores occur as

[14] Allan, *Trans 4m Electrochem Soc*, 41 239 (1922)
[15] Jones, "Tin Fields of the World," Mining Publications, Ltd, London, 1925
[16] Sixteenth Ann Report, U S Geol Survey (1896) The ratio still holds good in modern practice
[17] "Data of Geochemistry," *U S Geological Survey Bulletin*

acid-soluble basic sulfates, carbonates, oxides, or chlorides Cassiterite
has long been regarded as one of the most insoluble compounds known
There seems to be some geologic evidence, however, that there may
have been secondary enrichment of veins by solution, transportation,
and deposition of cassiterite

The following materials were treated with the same leaching
solutions

A Unground, unroasted Bolivian concentrates (hereafter termed
raw concentrates) of the following analysis

Component	Per Cent		Per Cent
Sn	67 95	which is equivalent to SnO_2	86 2
Fe	4 19	which is equivalent to Fe_2O_3	5 96
Sb	0 04		
As	0 01		
Cu	0 036		
Bi	0 296	which is equivalent to Bi_2O_3	0 33
WO_3	1 42		
SiO_2	1 73		
S	0 28		

B Raw concentrates of the above analysis pulverized in a ball mill
so that the average maximum particle size was 1 0 μ

C Unground roasted concentrates—particles retained on a 10-mesh
standard Tyler screen This material is the raw concentrates which had
been roasted in Duraloy or ferrochrome crucibles for three-quarters
of an hour at temperatures from 900° to 1100° C This roasted material
was in part magnetic and black in color in contrast to the red color of
the raw concentrates

D Stannic oxide of the J T Baker Chemical Co analyzed grade
Average maximum-occurring particle size was 1 8 μ

E Black stannous oxide of the J T Baker Chemical Co analyzed
grade Average maximum-occurring particle size was 1 5 μ

Leaching was done by weighing 10 grams of the substances into
flint-glass oil-sample bottles of 4-ounce capacity All determinations
were made in duplicate This resulted in the use of ten bottles for every
leaching solution, inasmuch as there were duplicate samples Each test
took 100 cc of the leaching solution The bottles were stoppered with
paraffined corks, wired in place to hold them during agitation The
agitation was provided by a shaft-and-clamp agitator, the bottles being
held in place in the jaws of universal clamps which were, in their turn,
clamped on to a ⅝-inch steel shaft, rotating at 36 to 38 r p m The
bottles were so placed that the ends traveled on the circumference of a
circle of 9-inch radius The shaft was driven by a one-eighth horse
power direct-current shunt-wound motor with a speed of 366 r p m ,
it was connected to the shaft by means of back gearing and a 16-inch

pulley on the shaft, so that there was a speed ratio of about 10 1 This speed was selected after experimental data showed that it was just slow enough to allow the particles to fall through the whole length of the bottle twice per revolution, and yet fast enough to keep the particles in constant agitation Agitation was continued for at least two weeks, twenty-four hours of the day Many of the solutions remained in contact with the solid materials for as long as six months to a year before analyses of the solutions were made All this work was done at room temperature of 20° to 25° C

Dissolution of the stannic oxide, if effected at all, may be presumed to take place in several different ways It may, perhaps, get into solution as a salt, such as a stannate, or, by reduction to the stannous form, in which it is fairly readily soluble, or by chemical reaction, in which the oxygen is replaced by another element, resulting in a soluble compound of tin The substances used for leaching may be divided into various classes

1—Strong acids, such as sulfuric or hydrochloric
2—Weak acids, such as acetic or oxalic
3—Strong bases, such as sodium hydroxide or barium hydroxide
4—Weak bases, such as ammonia
5—Salts, which may be divided into neutral, as sodium chloride, acid, as sodium acid sulfate, or basic—those resulting from a weak acid and a strong base, such as potassium cyanide
6—Oxidizing agents, such as chlorine or bromine
7—Salts which are reducing agents
   a Those whose reducing properties are due to the basic part of the salt, as ferrous sulfate
   b Those whose reducing properties are due to the acidic part of the salt, such as sodium sulfite
8—Salts which are oxidizers, divided into those whose oxidizing properties are found in the basic part of the salt, such as ferric chloride, and those whose oxidizing properties are found in the acidic part of the salt, such as sodium nitrate
9—Combinations of the above groups in many possible ways, such as neutral salts in saturated sulfur dioxide or saturated chlorine solution, to take merely one of many examples

It is interesting to note at this point that the soluble salts of tin are very limited in number Tin nitrate and tin cyanide do not exist Only the sulfates, halides, the sulfocyanate, and the chlorate are soluble among its inorganic compounds The complex thiostannites and thiostannates are soluble The organic salts, the acetates, oxalates, tartrates, and malates are soluble

Of the inorganic salts stannous sulfate very readily changes over in the presence of moisture to oxy- and stannic salts Stannic sulfate is very readily hydrolyzed in aqueous solution The fluorides of tin are quickly affected by moisture, with resultant decomposition All the

stannous halides readily oxidize to the stannic form, in neutral solutions they readily decompose to form cloudy solutions as a result of the formation of oxy-salts The thiocyanate and chlorate are fairly stable under proper conditions, but they readily hydrolyze in aqueous solution The organic salts of tin are readily decomposed, with the formation of metastannic acid or oxy-salts No tin salts exist which are as stable as copper sulfate, copper nitrate, or copper chloride Stannic chloride is a fuming liquid at ordinary temperatures, as $SnCl_4$ $5H_2O$ it is a solid readily affected by moisture and easily hydrolyzed in aqueous solution

The procedure used by the author for the determination of tin in leaching solutions resulting from the treatment of stannous oxide, stannic oxide, roasted, ground, and unground ores, was as follows

The oil sample bottles in which the materials had been agitated were unstoppered after the bottles had been washed on the outside Then the solution was filtered through qualitative filter paper, and 50 cc , carefully measured with a pipette, was taken for analysis Solutions were neutralized in those samples which were known to have excessive acidity and, in all cases, brought to concentration equivalent to 2 5 cc of hydrochloric acid per 100 cc of solution Tin was then determined quantitatively [18]

Results obtained with the various leaching solutions are tabulated in Table 5 The solubility of the leach constituents is given for reference Stannous oxide, previously known to be soluble in various reagents, is included in the data for comparison

As the investigation of the solubility of tin concentrates had as its aim the development of a leaching process, only such chemicals were used as are available in commercial quantities and at reasonable prices

The table shows that in no case was there marked solubility in a commercial sense In practically all cases the solubility of the concentrates was the same, irrespective of their previous treatment It did not make any difference in the solubility whether the concentrates were treated as received, or after roasting, or after fine grinding and screening

In some cases, notably those of $M/10$ ferric sulfate, $M/1$ ammonium chloride, and $M/1$ potassium cyanide, roasting the concentrates decreased the tin solubility

In a number of cases the solubility of the chemical stannic oxide is very much higher than the stannic oxide of the tin concentrates Stannic oxide is produced either by furnace oxidation of tin metal

[18] For the methods used, see Fink and Mantell *Eng Mining J* , 125 201 206 (1928)

TABLE 5

RESULTS OF TESTS SHOWING SOLUBILITY OF TIN OXIDE AND CONCENTRATES IN VARIOUS SOLVENTS

Leaching Solution	Solubility of Leaching Salt grams per 100 cc	Concentration of Leaching Salt grams per liter	Concentrates grams tin per liter in solution after leaching				
			SnO	SnO_2	Raw	Roasted	Ground
$FeCl_3$ $6H_2O$ $M/10$	246 0	27 0	1 04	0 05	0 04	0 05	0 05
$FeSO_4$ $7H_2O$ $M/10$	32 8	27 8	2 14	0 04	0 03	0 05	0 03
$Al(NO_3)_3$ $9H_2O$ $M/10$	very soluble	37 5		0 00	0 00	0 00	0 00
$(COOH)_2$ $M/10$		12 6	1 16	0 10	0 10	0 19	0 04
NaF $M/2$	4 0	21 0	1 85	0 25	0 13	0 10	0 10
$Fe_2(SO_4)_3$ $M/10$	very soluble	40 0	62 60	0 17	0 25	0 10	0 30
$MgSO_4$ $M/10$	26 9	24 7	0 41	0 00	0 04	0 02	0 01
Na_2SO_4 $M/10$	14 1	25 0	0 11	0 27	0 02	0 01	0 02
$KHSO_4$ $M/10$	36 3	13 6	2 07	0 22	0 05	0 06	0 01
NH_4Cl $M/1$	29 4	53 5	0 25	0 01	0 14	0 00	0 04
$SnCl_2$ $M/1$	118 7	225 7		Loss	Loss	Loss	Loss
$CaCl_2$ $M/1$	49 6	75 5	0 54	0 13	0 14	0 10	0 08
KCN $M/1$	122 0	65 0	0 27	0 05	0 30	0 10	0 15
26% NaCl, sat $PbCl_2$	260 0	260 0	1 10	1 03	0 27	0 29	0 08
HCOOH 20%		200 0	29 95	0 02	0 04	0 06	0 04
NaCNS $2M$	177 2	40 5		0 07	0 03	0 03	0 03
$HC_2H_3O_2$ $2M$, sat Cl_2		120 0	51 04	0 04	0 08	0 07	0 04
H_2SO_4 $2M$, sat Cl_2		196 0	139 35	0 48	0 04	0 03	0 04
I_2, sat	0 18	3 0	0 84	0 06	0 08	0 08	0 06
Br_2, sat	4 17	16 0	3 07	0 08	0 10	0 10	0 04
NaCl, $M/2$, sat Cl_2	29 3	29 0	0 55	0 20	0 12	0 10	0 11
NH_4Cl $M/1$, sat SO_2	29 4	53 5	0 24	0 07	0 04	0 06	0 05
$(NH_4)_2SO_4$ $M/1$, sat Cl_2	71 0	13 2	8 86	0 03	0 02	0 03	0,05
$FeCl_3$ $M/1$, sat Cl_2	246 0	162 4	24 04	0 18	0 13	0 11	0 11
$MnSO_4$ $M/1$	53 2	151 0	3 40	0 04	0 03	0 02	0 02
Na_2SO_4 $M/3$, sat SO_2	5 02	47 3		0 07	0 03	0 02	0 04
$NaHSO_3$ $M/1$		104 0		0 10	0 07	0 03	0 04
NaCl $M/2$, sat SO_2	35 70	29 25		0 10	0 03	0 02	0 03
$NaHSO_3$ $M/1$, sat SO_2		104 0		0 14	0 07	0 03	0 03
$NaHSO_4$ $M/1$, sat SO_2	50 0	120 1	1 10	0 50	0 09	0 06	0 06
$NaHSO_3$ $M/1$, NaOH $2M$			5 38	2 05	0 07	0 07	0 07
$(NH_4)_2S$ $M/1$	100 0	68 2	0 31	0 31	0 16	0 09	0 10
$NaHSO_4$ $M/1$, sat Cl_2	50 0	120 1	28 30	0 30	0 09	0 11	0 09
$CuSO_4$ $M/2$	20 0	79 8	1 15	0,50	0 05	0 04	0 04
Na_2S_x, sat	20 0	160 0		162 00	0 80	0 70	0 75
Na_2S, sat	15 4	154 0		31 36	0 87	0 74	0 68
Aero Cyanide (50% NaCN) sat		100 0	0 30	1 07	0 06	0 03	0 06
H_2SiF_6 20%		200 0		0 47	0 42	0 21	0 21
H_2SO_4 15%, NaCl 5%		150 0	125 00	5 41	0 89	0 70	0 26
H_2SO_4 30%, $FeSO_4$ 30%, NaCl 5%			132 50	3 50	0 50	0 60	0 52
H_2SO_4 10%, NaF 4%			140 00	0 38	0 45	0 47	0 42
H_2SO_4 20%, NaF 4%			140 20	0 40	0 42	0 38	0 25
$FeSO_4(NH_4)_2SO_4$ $6H_2O$ $M/2$, sat SO_2		196 0	1 56	0 17	0 20	0 20	0 10
HCOOH 10%		100 0	20 59	0 09	0 09	0 08	0 07

or by chemical oxidation (such as through the use of nitric acid) of tin metal or tin salts

It seems evident that the stannic oxide produced by chemical processes is a material with quite different properties from the stannic oxide of cassiterite The stannic oxide of cassiterite is markedly crystalline, the crystals being of comparatively large size Cassiterite occurs in igneous rocks and was formed at 1132° C, or above the fusion point The chemical stannic oxide is an amorphous material, non-crystalline in its nature It is produced far below the fusion point The stannic oxide used in these experiments was roasted but not fused

The results were studied and re-assembled in various ways in an attempt to determine whether any particular radicals were more active in causing solution than were others From the results tabulated it can be seen that the sulfate ion causes no great amount of solubility The effect of chlorides and fluorides as well as greater acidity of the leaching solution is shown in the increased solubility The examples of this are ferric sulfate $M/10$, sulfuric acid 15 per cent, sodium chloride 5 per cent, sulfuric acid 30 per cent, ferrous sulfate 30 per cent, sodium chloride 5 per cent, and the similar series following

The chlorides cause an increase in the solubility of stannic oxide and of the concentrates In those cases where the ammonium ion was present, the solubility decreased The effect of sulfur dioxide and chlorine may be seen in the case of NaCl $M/2$ saturated with Cl_2 and the same solution with SO_2 substituted for the dissolved chlorine Solubility of the concentrate decreases markedly Of all the compounds studied, the chlorides have the greatest solubility effect on the concentrates

Iron salts *per se* do not seem to dissolve cassiterite The combination of relatively strong acidity, an iron salt, and a chloride gave the best solubility of those iron salts tested Ammonium salts do not have appreciable solvent action on Bolivian concentrates

F R Koeberlein [19] recently described some deposits of cassiterite in which, according to field evidence, it appears that much secondary cassiterite was deposited under conditions resembling those found in the zone of secondary sulfide enrichment Facts observed in the field seem to uphold the conclusion that the solution of cassiterite in the tin veins and redeposition at lower levels, far from being a scientific curiosity, is a natural process of the most vital economic importance in Bolivia

[19] "Geologic Features of Bolivia's Tin Bearing Veins," *Eng Mining J-Press*, 121 636 (1926)

Geologically the solubilities of cassiterite observed in this work are appreciable The solubilities observed seem to support the solution theory of enrichment This theory supposes that there is solution of cassiterite in the upper parts of the vein, downward percolation, and redeposition of tin oxide at lower levels That there are objections to this theory is obvious when placer cassiterite deposits are considered This mineral is carried many miles from its source, in the finest state of comminution, subject to attack by waters of various and varying alkalinity and activity Cassiterite is usually considered to be extremely inert and insoluble Chemically this is true, geologically it is appreciably soluble

Koeberlein makes the suggestion that the oxidation of associated pyrite has a reducing action on stannic oxide, facilitating its solution in the form of compounds of lower valence It has been shown that in acid solutions sulfur dioxide oxidizes stannous oxide, it would not, therefore, reduce stannic oxide, and the suggested explanation must be modified Elsewhere the presence of copper minerals is cited as having a possible effect, the low solubility of Bolivian concentrates in copper solutions does not seem to support this statement

On the whole, the values found for the solubility of tin compounds from Bolivian concentrates may bulk large from a strictly geologic viewpoint

Reprecipitation of tin salts may occur easily, as a consideration of the properties of the soluble tin salts will show The halides of tin are readily hydrolyzed, the decomposition proceeding more rapidly with increase of temperature These salts in their lower valence forms are readily oxidized The other soluble tin salts easily decompose None are as stable as the copper salts

Experiments carried on in attempted leaching of cassiterite by a large number of different reagents at room temperature showed that

1—Cassiterite is very insoluble

2—No cheap chemical compound has any appreciable effect on cassiterite

3—No cheap chemical compound was found which, from the results obtained, held out the opportunity or possibility of a leaching process

Further experimental work was carried on at higher temperatures with aqueous solutions of the mineral acids at various concentrations alone, and with various salt additions The salt additions were made to the concentrates, the acids were then poured on the concentrates, and the mass was well stirred

This work is reported in brief form because of the negative results obtained In all cases, five grams of ore were digested with 500 cc of the solution in question at 100° C for four hours, except where otherwise noted In many cases the concentrates were disintegrated and iron was leached out The concentrates had been previously roasted They were ground in a ball mill to pass a 24-mesh screen After digestion, the solution was cooled, filtered, and tested qualitatively for tin The method used was first to reduce with zinc and then test 50 cc of the solution with 10 cc of a 1 per cent solution of mercuric chloride If a definite blackening of the white mercurous chloride precipitate occurred, the test was called positive and the tin content of the solution was thus shown to be greater than 0 8 gram tin per liter

Using the above test, no positive results were obtained with the following solutions

1*A*—Concentrated sulfuric acid, specific gravity 1 836 In testing for tin, this solution was diluted to 25 per cent, then tested and calculated back to its original concentration No hydrolysis of tin salts was observed Tests negative Determinations made at 100°, 120°, 140°, and 180° C
2*A*—50 per cent sulfuric acid, diluted for testing as 1*A*
2*B*—2*A* plus 2 per cent NaF
2*C*—2*A* plus 2 per cent NaCl
2*D*—2*A* plus 5 per cent NaCl
2*E*—2*A* plus 2 per cent NaNO$_3$
  All tests negative No precipitate with HgCl$_2$
3*A*—25 per cent sulfuric acid
3*B*—3*A* plus 2 per cent NaF
3*C*—3*A* plus 2 per cent NaCl
3*D*—3*A* plus 5 per cent NaCl
3*E*—3*A* plus 2 per cent NaNO$_3$
3*F*—3*A* plus 5 per cent Fe$_2$(SO$_4$)$_3$
  All tests negative
4*A*—50 per cent hydrofluoric acid Copper dish used Time of digestion, one hour Temperature 75° C
4*B*—4*A* plus 5 per cent NaCl Glass beaker used Temperature 75° C Time of digestion, one hour
4*C*—4*A* plus 10 per cent Na$_2$SO$_4$ Temperature 75° C
4*D*—4*A* plus 2 per cent NaNO$_3$ Temperature 75° C
  All tests negative
5*A*—Concentrated hydrochloric acid (38 per cent) Temperature 100° C Time, four hours
5*B*—5*A* plus 2 per cent NaNO$_3$
5*C*—5*A* plus 5 per cent NaF
5*D*—5*A* plus 5 per cent NaCl
5*E*—5*A* plus 2 per cent Na$_2$SO$_4$
  All tests negative
6*A*—30 per cent NaOH
6*B*—6*A* plus 2 per cent NaCl
6*C*—6*A* plus 2 per cent NaF
6*D*—6*A* plus 2 per cent NaNO$_3$
6*E*—6*A* plus 5 per cent NaCl
6*F*—6*A* plus 5 per cent Na$_2$SO$_4$
  All tests negative as defined above
7*A*—20 per cent solution of ferric sulfate Temperature 100° C Time, four hours Tests negative

These results do not offer much encouragement for the immediate development of a leaching process

REDUCTION OF TIN CONCENTRATES BY ALUMINUM

Fink and Mantell studied the application of the "thermit" reaction, which is reduction by aluminum, to tin concentrates [20] The reaction is represented by the equation

$$3SnO_2 + 4Al = 3Sn + 2Al_2O_3$$

Calculated from the reaction, the proportions are 453 parts stannic oxide to 108 parts of aluminum, which gives 357 parts of tin This is approximately $3\frac{1}{4}$ pounds of tin per pound of aluminum With an ore of 60 per cent tin content, on the basis of the tin alone, about one part of aluminum would be required for five parts of ore Because of the iron and other metals present which are aluminothermically reduced, and to allow excess aluminum for the reaction, a proportion of four parts of ore to one of aluminum was used

There is a decided difference in the specific gravities of molten alumina and liquid tin There is also a decided difference in specific gravity between the gangue of the tin ore and the liquid tin The specific gravity of the gangue is very much closer to that of alumina than to the liquid tin As a result, on cooling, a very good separation was made of the combined alumina and gangue from the heavier liquid tin A sharp line of demarcation defined the solidified slag and the tin metal Examination of the slag, after crushing, showed that it was almost entirely free of tin prills

The tin metal was clean It liquated easily In liquation there was considerable amount of dross which could be shown to be caused by an excess of aluminum metal used in the reduction

Ample evidence was deduced to indicate that, with further study and development, the tin yield from the concentrates could be made almost quantitative The process would have the advantage of producing clean metal, easily liquated, with little other slag save that of the aluminum oxide The thermodynamics of the reaction are

$$Sn + O_2 = SnO_2 + 141,300 \text{ calories}$$
$$2Fe + 3/2O_2 = Fe_2O_3 + 195,600 \text{ calories}$$
$$3SnO_2 + 4Al = 3Sn + 2Al_2O_3 + 361,300 \text{ calories}$$
$$2Fe_2O_3 + 4Al = 4Fe + 2Al_2O_3 + 394,000 \text{ calories}$$
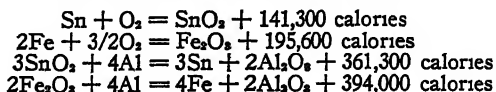
This shows the reaction to be of the same order of magnitude as the Goldschmidt thermit reaction

Eng Mining J 125 325-328 (1928)

It is interesting to note in that connection that aluminum and iron are stated by Gwyer [21] to be completely miscible in the liquid phase On cooling, mixed crystals are formed having the composition of 40 to 48 per cent iron and 66 to 100 per cent iron with an iron-aluminum compound formed which has a melting point of 1145° C If this compound be more readily or more easily formed than the iron-tin alloys or hardhead compounds, the aluminum will thus act as a scavenger for iron in the tin metal, producing a tin more free from iron than that produced by any method in which aluminum metal is not used

The economics of aluminum reduction of tin are not encouraging Approximately three pounds of tin may be produced per pound of aluminum At a current price in the United States of 25 cents per pound of virgin aluminum, the cost per pound of smelting tin with aluminum would be 8⅓ cents With scrap sheet aluminum at 14 to 16 cents per pound, this means an expenditure of 5 cents per pound of tin This is equivalent to a cost of $66 per long ton of 60 per cent tin concentrate, as compared with $50 by the ordinary carbon reduction method

A substitution of zinc for aluminum, on the approximate basis of a pound of tin per pound of zinc, with scrap zinc at 4 cents per pound, gives an estimated expenditure of $52 80 per ton of 60 per cent concentrate

Metallic reduction of tin concentrate may be of use in localities where tin deposits are too small to warrant a smelter or a reduction furnace Reduction by aluminum or zinc requires practically no equipment The method may be applicable in some locations As a general smelting method, it does not show promise at present prices for aluminum

REDUCTION OF STANNIC OXIDE BY OTHER METALS

Metallic iron does not reduce stannic oxide in the solid phase at the maximum temperatures obtainable in small tube furnaces heated by chromel resistors

A mixture by weight of 50 per cent C P ignited stannic oxide and 50 per cent finely powdered metallic iron (hydrogen-reduced) was made. The materials were thoroughly mixed by grinding

Several charges were heated to 900° to 950° C and held there in a nitrogen atmosphere for ¼ to 1 hour Chemical analysis of the material showed no tin, and no tin globules were observable under the

microscope Two additional runs duplicating the conditions of the above were made, with the same results of lack of reduction of the stannic oxide by the metallic iron

It was not to be expected that there would be a reducing reaction between two solid phases, as in the case of the two powders, in an inert gas atmosphere The experimental data show that solid finely divided iron is without reducing action on solid stannic oxide It follows that it would not be expected that iron in the solid phase would exert any reducing effect on cassiterite

It is known that iron in the liquid phase has reducing action on molten stannic oxide with the formation of the iron-tin alloy, hardhead This material, one of the banes of the tin-smelters' existence, is formed above 1132° C, the melting point of stannic oxide

If temperatures of furnace operation be such that neither stannic oxide nor metallic iron is in the molten condition, the tendency to form hardhead should be lessened It is well known that the rate of alloying between tin in the liquid phase and iron in the solid phase is slow in comparison with the reaction when both are in the liquid phase Gaseous reduction (economical at 750°) operates at temperatures well below the melting points of either stannic oxide or metallic iron Hardhead troubles should, therefore, be considerably reduced in gaseous reduction Experimental evidence shows this to be true

Molten bismuth, at temperatures not much above its melting point, has no reducing effect on stannic oxide Bismuth compounds are usually constituents of Bolivian tin concentrates Such compounds, and among these the oxides, are more readily reduced than is stannic oxide by reducing agents

Similar determinations were made in the case of lead and copper, at temperatures just above their melting points

The thermophysics of these reactions are as follows [22]

$$Sn + O_2 = SnO_2 + 141{,}300 \text{ calories}$$
$$Pb + O = PbO + 50{,}800 \text{ calories}$$
$$Pb + O_2 = PbO_2 + 63{,}400 \text{ calories}$$
$$2Bi + 3O = Bi_2O_3 + 139{,}200 \text{ calories}$$
$$2Fe + 3O = Fe_2O_3 + 195{,}600 \text{ calories}$$
$$Fe + O = FeO + 65{,}700 \text{ calories}$$
$$Cu + O = CuO + 37{,}700 \text{ calories}$$
$$SnO_2 + 2Fe = Sn + 2FeO - 900 \text{ calories}$$
$$3SnO_2 + 4Fe = 3Sn + 2Fe_2O_3 - 32{,}700 \text{ calories}$$
$$SnO_2 + 2Pb = Sn + 2PbO - 39{,}700 \text{ calories}$$
$$SnO_2 + Pb = Sn + PbO_2 - 77{,}900 \text{ calories}$$
$$3SnO_2 + 4Pb = 3Sn + 2Pb_2O_3 - 175{,}000 \text{ calories}$$
$$3SnO_2 + 4Bi = 3Sn + 2Bi_2O_3 - 145{,}500 \text{ calories}$$

[22] Richards, "Metallurgical Calculations," New York, McGraw Hill Book Company, Inc, 1918

Molten lead, bismuth, and copper aie without marked reducing action on stannic oxide In the reduction of a concentrate the oxides of these metals will consume the ieductant The reduced metals do not in turn reduce tin oxides with which they are in contact

EFFECT OF IRON AND BISMUIH OXIDES ON MELIING POINT OF STANNIC OXIDE

Bolivian vein-tin concentrates contain a large number and amount of impurities Those which are most important are the compounds of iion and bismuth Ordinaiily concentiates of vein oiigin fuse at lowei temperatures than those of alluvial oiigin, owing to the greater impurities of the original veins and the difficulty of dressing vein oies

To determine the effect of iion and bismuth oxides on the melting point of stannic oxide, samples were made containing these materials in the proportions in which they occur in the concentiates

Melting-point determinations were made following the American Society for Testing Materials [28] procedure for deteimination of the fusibility of coal ash, using the furnace arrangement as recommended for this work The furnace was operated with a minimum amount of excess air The results are given in Table 6 The paiticle size of maximum occurience was 3 μ

TABLE 6

MELTING-POINT DETERMINATIONS ON SIANNIC OXIDE

Material	Softening Temperature, °C	Initial Defoimation Temperature, °C	Fluid Temperature or Melting Point, °C
Fe_2O_3	1,492	1,497	1,503
SnO_2	1,120	1,125	1,130
SnO_2 94 35% } Fe_2O_3 5 65% }	918	925	932
SnO_2 99 01% } Bi_2O_3 0 99% }	841	854	863

It is illuminating to see how gieatly the small amount of bismuth oxide affects the melting point of stannic oxide As ferric oxide has a higher melting point than bismuth oxide, the effect, though large, is less marked

These determinations give some insight into the effect that the oxides of iron and bismuth have on the fusion point of tin concentrates In gaseous reduction, the operation depends upon the absence of slagging until complete reduction is effected It can be seen that with ores high in bismuth oxide, means may have to be employed to counter-

[28] *Am Soc Testing Materials Standards*, 1924, p 994, also Fieldner, Hall and Field, *Bur Mines Bull* No 129

act the lowering of the melting point of the concentrates Experimental work has shown us that small amounts of lime up to 1 per cent by weight of the charge are very effective in raising the melting point to prevent undesired slagging of the material

One of the methods that have been proposed for the winning of tin from Bolivian concentrates consists of the following steps

1 Reduce the concentrate by gaseous reduction

2 Leach the reduced concentrate with a solution low in tin It is preferable that this solution be a good electrolytic refining agent

3 Electrolytically precipitate the tin metal under controlled conditions, so that "electrolytic tin" of high purity be obtained

4 Re-use the electrolyte now stripped of some of its tin for leaching fresh, reduced concentrate The electrolyte then operates in a closed cycle

Commercial practice prefers a cheap, simple, and economical refining electrolyte These conditions are satisfied by the sulfuric acid-sodium sulfate-stannous sulfate bath [24]

Leaching solutions which have the possibility of being good refining baths are limited in number Additions of sodium sulfate to 15 per cent sulfuric acid do not markedly increase its solvent power for tin, although the sulfate may decrease hydrolysis of tin salts in solution Good conditions for the tin-refining bath call for a tin concentration of 35 grams per liter Additions of sodium chloride to 15 per cent sulfuric acid increase its solvent power sufficiently to obtain this concentration

A satisfactory leaching solution for tin metal, and therefore presumably for reduced tin concentrates, contains 15 per cent sulfuric acid and 5 per cent sodium chloride [25]

Work on a semi-commercial scale on tin concentrates reduced by hydrogen showed that all of the reduced metal was quantitatively soluble in hydrochloric acid or sulfuric acid plus sodium chloride Low temperature reduction could be complete and the tin metal produced could be completely recovered On small samples at least, 100 per cent metal recovery (in solution form) from the concentrates can be obtained

Results from a large number of leachings of gaseous-reduced concentrates show tin recoveries from 95 to 98 per cent This work was not carried further, as the results obtained would mean little save as indications as to what might be expected in practice There is little doubt that with counter-current leaching and continuous electrolytic

[24] U S Pat 1,466,126 See "Electrolytic Refining," p 157 on
[25] Fink and Mantell, *Eng Mining J*, 125 452 455 (1928)

precipitation of metal and re-use of leach liquor, tin recoveries higher than 96 per cent are entirely possible Of course, iron will build up in the leach liquor, with the resultant necessity of constantly bleeding some of the liquor Bismuth, copper, and other metals would also build up in plant operation

Leaching efficiencies would depend upon many factors, such as size, type, and shape of apparatus, and method of leaching Higher metal recoveries than those obtained from smelting are to be expected, as the operation consists of leaching a loose, sandy mass containing more than 80 per cent of an easily acid-soluble metal

Reduced tin concentrates were leached in place with simultaneous deposition of the metal electrolytically The results did not seem to hold out hope for a commercial process which would leach reduced ore in place with simultaneous electrodeposition

Leaching with agitation separately from electrolytic precipitation is decidedly preferable to leaching and electrolytic precipitation at the same time The first method gives very much higher yields, at higher current and energy efficiencies, with the production of better cathode deposits The metal is more compact, is better looking, and is more easily handled

Gangue from the leaching treatment was clean Under a microscope it showed quartz, garnet, and tourmaline There was no fusion of the tourmaline at the temperatures at which the gaseous reduction took place The temperature of operation is such as to eliminate entirely the problem of the low-fusing constituents covering over the particles of cassiterite and prevent the reducing gas from coming in contact with the material, thus not allowing its reduction to metallic tin

Wells [26] proposed zinc and hydrochloric acid as a means of dissolving cassiterite for analytical purposes The zinc when in contact with the particle of cassiterite reduced it as a result of the hydrogen generated This is the present-day field test An investigation of the possibility of commercial development of this phenomenon shows that the energy efficiency of the process is so low as to make the idea impracticable

Tin metal has been known not to be readily soluble in sulfuric acid As a result of studies on the solubility of tin metal and the various constituents of a sulfuric acid tin-refining bath, the important effect of chloride-ion addition on the tin solubility has been shown

It is believed that gaseous reduction of tin concentrates offers great promise Slag troubles are eliminated Refractory troubles are not in

evidence Formation of hardhead is decreased The operation is one of low temperatures (750° C) Using hydrogen generated by electrolytic means and electrical heating, the total power requirements are 1,930 kilowatt-hours per ton of 60 per cent concentrate

The combination of gaseous reduction, leaching the reduced charge, and electrolytically precipitating the tin metal offers a cheap method of dealing with foul Bolivian ore with the production of tin metal of 99 98 per cent purity It is believed that tin recoveries 95 per cent or better are possible by this combination of steps The cost to produce "electrolytic tin" from a ton of 60 per cent Bolivian concentrate is estimated, with power at $0 01 kilowatt-hour, to be about $20 14 per 1,200 pounds of metal, or $35 40 per ton of finished metal This is based on 1,030 kilowatt-hours for hydrogen production per ton of 60 per cent concentrate, 900 kilowatt-hours for heating to 750° C , and 144 kilowatt-hours per ton of tin to be refined electrolytically at 0 3 volts, 85 per cent current efficiency, at 10 amperes per square foot This cost compares exceedingly well with carbon reduction smelting costs at $40 to $50 per ton of 60 per cent concentrate With cheaper hydroelectric power, say at $0 003 per kilowatt-hour, the cost for hydrogen reduction, leaching, and precipitation would be approximately $6 05 per ton of 60 per cent concentrate

Smelters can handle foul Bolivian ores only with great difficulty Without electrolytic refining it is difficult even to produce "standard" metal Hydrogen reduction, leaching, and electrolytic precipitation offers a cheaper method, with greater ease of operation , moreover, it is capable of producing the highest grade of metal from complex and foul ores

CHAPTER 8

ELECTROLYTIC REFINING

Electrolytic tin is a relatively new arrival in the family of pure metals Its development has progressed in the face of difficulties and opposition, much of which is upon an unfounded basis

The use of the electrolytic process for the winning of metals from low-grade ores (too poor in metal content to warrant consideration for smelter charges, but high enough so that by leaching and electrolytic processes large-scale operators are able to produce metal at lower production costs than the smelters of high-grade ores) is too well known in the case of copper, silver, etc , to warrant any discussion here

The metallurgy of copper has been worked out in great minuteness and detail, in contrast the metallurgy of tin is a virgin field The tin resulting from thermal methods can be refined to a degree of purity sufficient for most purposes by ordinary dry methods, such as drossing and liquation These are simple processes which are entirely satisfactory for the metal resulting from the reduction of pure ores, such as those produced in the Straits Settlements and mines in that vicinity, which produce the well-known Banka and Billiton brands of tin

The production of pure ores from alluvial deposits is constantly decreasing This is the source from which pure tin metal can be most easily produced by straight fire methods The production of vein ores (such as Bolivian), highly contaminated with undesirable impurities, is constantly increasing to make up for the decreases of "stream" or alluvial tinstone, and to produce metal to satisfy the annually increasing demand

The tin metal produced from straight metallurgical processes from impure ores is at best a very impure form containing Pb, As, Sb, Fe, Cd, and Cu as impurities from which it must be refined The usual methods are by (1) liquation, (2) boiling, or (3) tossing In liquation, advantage is taken of the low melting point of tin Impure metal is heated on the inclined bed of a furnace to a temperature just above its melting point Comparatively pure tin trickles down to a basin below, leaving higher-melting-point impurities on the bed of the furnace. Liquation will not remove readily fusible lead and bismuth

mpurities, these are removed by boiling or tossing Both of these are oxidizing methods The first is similar to the "poling" operation of the copper refinery, the second consists of pouring ladlefuls of molten metal from a height back to the bath of metal The metal is then allowed to stand in the liquid state for several hours to allow gravity separation of the remaining heavier impurities

From operations such as drossing, boiling, tossing, or liquating, it is obvious that a tin metal of a quality equivalent to electrolytic copper or nickel can not be produced In 1906 Blount[1] was among those to recognize the great desirability of producing electrolytically a purer metal than the commercial pure tin containing 0 50 to 1 00 per cent impurities In the manufacture of high-grade non-ferrous alloys, particularly bronzes, solders, and gun metal, a pure metal is distinctly preferable to one containing miscellaneous alien substances Nevertheless, in 1906 electrolytic tin had no industrial existence Throughout the literature from that time until 1917 statements were made that there was no field for the electrolytic process for the refining of tin, as metallurgical processes produced tin in a sufficiently pure condition for ordinary uses, and extremely pure metal had no particular sale[2] Seemingly, electrolytic tin must overcome the same series of useless prejudices and adverse propaganda that electrolytic nickel and copper met and conquered There is no question that electrolytic refining will produce a purer product than thermal methods, that the purer metal allows the production of higher-grade non-ferrous alloys, that many manipulative difficulties in the application of tin metal vanish when the deleterious impurities are no longer present, and that electrolytic processes can be used to obtain pure metal from the decidedly impure or "foul" Bolivian ores, from which straight dry thermal methods of refining produce only a poor grade of metal

ELECTROLYTES

Many electrolytes for tin refining have been proposed Some of them have been used on a commercial scale, others have found application only for plating, and a multitude of others so violated commercial considerations that they have never been used

In the selection of a salt for any refining process, the following conditions will weigh The acid radical must be fairly cheap and stable The salt must be soluble If impurities are to be taken out as slime, they should be insoluble in the electrolyte used The tank lining should

[1] Blount, "Practical Electro Chemistry," New York, Macmillan, 1906, p 124
[2] Allmand, "Principles of Applied Electrochemistry," New York, Longmans, Green and Co, 1912, p 287, *also* 1924, p 329

not be affected by it Poisonous fumes should not be given off, and the cathode should not readily redissolve

Plating stands on a little different ground in that it is a quality process Therefore the cost of the salt used is not vital and in small operations poisonous fumes may be controlled

In the special field of tin refining, it is necessary to have an electrolyte in which the tin compounds formed are very soluble The tin concentration of the electrolyte must be great enough for the current density used As in copper refining, the electrolyte must be circulated to avoid segregation and polarization The use of a warm electrolyte results in lower voltages and more even anode corrosion A very desirable electrolyte, however, would be one that functioned satisfactorily at room temperature, thus eliminating the necessity of external heating The presence of suitable addition agents tends to cause smooth dense coherent cathode deposits

Tin electrolytes must be free from metal ions electronegative to tin, otherwise the other metals will plate out with the tin

One of the oldest electrolytes used for tin refining is the sodium-sulfide bath of Claus and Steiner [8] This bath was used commercially at Bootle, England, for several years The electrolyte consisted of a 10 per cent solution of sodium sulfide with dissolved sulfur Smooth deposits were obtained below 0 2 volt, above which hydrogen was evolved and spongy deposits formed Peruvian metal of 93 per cent tin content was refined to a 99 9 per cent material The electrolyte had to be kept uncontaminated from foreign metals either suspended or dissolved No circulation was possible as the anode mud would foul the solution The current could not be interrupted during a run, otherwise the polarization current would oxidize the cathode In his study, Neuman [8] found that in the refining of tin in sodium-sulfide solution the metal separates at the cathode as a smooth, dense deposit with a current yield of 98 to 99 per cent (calculated on tetravalent tin), when a current density of 1 ampere per square decimeter (10 amp /sq ft) is employed With a current density of 2 amperes per square decimeter (20 amps /sq ft) or more, evolution of hydrogen occurs, the deposit of tin on the cathode is spongy, and the current yield falls The sodium sulfide content in the electrolyte must not be allowed to fall below 10 per cent, otherwise a spongy deposit of tin is formed In sodium sulfide solutions containing sodium hydroxide, the current yield is over 100 per cent owing to the discharge of some Sn^{++} ions Free sulfur in the electrolyte

[8] Alkaline Sulfide Bath *Z Electrochem*, 15 33 6, 63 5 (1909), Steiner, *Electrochem Met Ind*, 5 309-12 (1907), Fisher, *Z anorg Chem*, 42 63 (1904), Neuman, *Z Electrochem*, 27 256 68 (1921)

forms polysulfide, which dissolves the tin and hinders its deposition
Initially the electrolyte must contain at least 0 6 per cent tin dissolved
as stannic sulfide The temperature of the electrolyte should be main-
tained above 80°, below 70° evolution of hydrogen sets in and the
cathode becomes coated with a gray-black spongy deposit With anodes
of alloys of tin with lead, iron, bismuth, silver, copper, and phosphorus,
these metals are converted into sulfides which settle as anode slime,
the tin deposited on the cathode being completely free from them
Arsenic is not deposited with the tin on the cathode, but antimony
is, if the current density be over 0 1 ampere per square decimeter
(1 amp /sq ft) For commercial usage this bath is difficult to work,
hard to control, disagreeable in operation, without compensating advan-
tages over competitive baths

ALKALINE BATHS

The alkaline baths[4] studied by many workers consisted of
$SnCl_2$ $2H_2O$ dissolved in sodium hydroxide A typical electrolyte is
that of Beneker, which consisted of 125 grams (16 66 oz /gal) sodium
hydroxide, 50 grams (6 66 oz /gal) stannous chloride, and 75 grams
(10 oz /gal) sodium thiosulfate per liter The alkaline baths when used
for refining tend to produce spongy and non-adherent cathode deposits
The baths are none too stable, oxidizing by the action of the air to
stannates and insoluble stannic acids The anode corrosion is greater
than the cathode deposition The cathode deposits are difficult to handle
and cause large losses in melting down to a compact form The bath is
operated at 80° C (176° F), with a current density of 10 amperes per
square foot (1 amp /sq dm) With current densities as low as 2
amperes per square foot (0 2 amp /sq dm), a fairly compact cathode
deposit may be obtained Straight alkaline baths are not now used for
tin refining but find application in electrolytic detinning and tin plating

Mathers and Bell, working with a bath of 60 grams crystalline stan-
nous chloride, 60 grams sodium hydroxide, and 1 gram of an addition
agent per liter, found that continued satisfactory deposits could not be
obtained even with a current density as low as 4 7 amperes per square
foot, due to gradual oxidation of the sodium stannite No satisfactory
method of prevention of oxidation, or of regeneration of the bath, was
found

Tin anodes in alkaline baths have a decided tendency to acquire

[4] Alkaline Baths *Metal Ind* 14 200 1 (1916), *Trans Am Electrochem Soc* 29 405
(1916), *Metal Ind* , 18 361 2 (1920), Hollard, *Bull soc enc ind nat* , July, 1912, Mennicke,
"Metallurgie des Zinns," Halle, Wm Knapp, 1910, Hughes, *Beama*, 10 138 41 (1922),
Mathers and Bell, *Trans Am Electrochem Soc* , 38 135 (1920)

passivity, at which time anode corrosion stops Such a state of affairs cannot be tolerated in any metal-refining bath

ACID BATHS [5]

A number of patents have been granted in various countries for tin-refining baths using the tin salts of organic acids such as acetic, formic, tartaric, citric, oxalic, and the tin salts of phosphoric and boric acids All of these have the objection that the electrolyte is expensive, easily decomposed, the solutions may be unstable, and the electrolytes must be kept pure These baths have been found useful for electrotinning but not at all for electrorefining

CHLORIDE BATHS [6]

There have been proposed many baths applicable to tin refining which make use of the solubility of stannous and stannic chlorides Among these may be mentioned that of Brand consisting of about 1 per cent by weight of concentrated hydrochloric acid and 9 per cent of stannous chloride Neutral or acid solutions of stannous or stannic chlorides produce coarse crystalline cathode deposits It has been claimed [7] that "beautiful dense deposits of tin can be obtained without the evolution of hydrogen by electrolyzing a NaCl SnCl$_2$ solution with low current density at ordinary temperatures " This holds true only for a short while, in continuous operation crystals and trees are produced which short circuit the electrodes The chloride baths have been advocated for use in diaphragm cells, but diaphragms in commercial refining introduce an undesirable cell complication and an increased voltage drop across the cell

FLUOSILICATE BATHS [8]

The successful application of hydrofluosilicic acid as an electrolyte for lead refining caused workers to attempt to apply it to tin, a more or less related metal It was early realized that the addition of small amounts of sulfuric acid in the bath would prevent electrolyte contamination by causing the formation of insoluble lead sulfate which rapidly fell out of the solution and became part of the slimes Some of the laboratory workers on the problem shortly worked out suitable

[5] Acid Baths Mathers and Cockrum, *Metal Ind* 14 252 3 (1916), Pasztor, *Electrochem Z* 16 281-5 (1910), German Pat 276,181 (1912), Battle, U S Pat 1,202,149, Marino, British Pat 11,011 (1915), Delahaye, French Pat 484,148 (1917)
[6] Chloride Baths (Brand Bath) Schnabel Louis, "Metallurgy," New York, Macmillan, 1907, vol II, p 549, Quintaine, Brit Pat 5,496 (1900), Feith, German Pat 205,051 (1907), Michaud and Delasson, French Pats 16,388 and 435,936 (1912), U S Pat 1,124,315
[7] *Bull Soc enc ind nat*, July, 1912, p 28
[8] *Eng Mining J*, May 27,1916, Hollis, U S Pat 916,155, Mennicke, U S Pats 799,091, and 779,092, Mathers, U S Pat 1,397,222, A S and R Co, French Pat 479,569 (1916), Schulte, U S Pat 1,423,686, Whitehead, U S Pat 1,157,830, *Elec Rev West Electricity*, 68 507 (1916), Vail, *Eng Mining J*, 101 927-9 (1916)

addition agents without which an entirely satisfactory electrode deposit could not be obtained Kern [9] experimented to find the best current density, addition agent, and electrolyte for use in the electrolytic refining of impure tin bullion so as to obtain tin as an adherent, dense, compact cathode The anodes used were 10 cm (3 937 in) long, 4 4 cm (1 73 in) wide, and 0 94 cm (0 37 in) thick. They contained 96 per cent tin, 0 5 per cent iron, 0 1 per cent arsenic, 0 2 per cent antimony, 2 0 per cent lead, 0 6 per cent copper, 0 1 per cent bismuth, and 0 5 per cent silver The cathodes were made of sheet tin 0 4 mm (0 0157 in) thick and were larger than the cathodes by 0 6 cm (0 236 in) on each of the two edges and bottom Electrolytes of stannous chloride, sodium stannous chloride, magnesium stannous chloride, sodium stannous fluoride, stannous fluosilicate, and a mixture of acid solutions of stannous fluoride and fluosilicate were tested Each solution contained 100 grams of tin per 100 cc Stannous fluosilicate is the best of the electrolytes which were tried It was found that addition agents were necessary for dense, adherent deposits of tin Aloin caused the formation of the best deposits when added to stannous fluosilicate electrolytes to the amount of 1 gram of aloin per 500 cc of electrolyte Peptone gave good deposits in many cases, while the others, except in stannous fluosilicate electrolytes, did not improve the deposits With current densities of 12 and 24 amperes per square foot (1 2 and 2 4 amps /sq dm) in many cases similar results were obtained

In the first commercial tin-refining plant in the United States—that of the American Smelting and Refining Company at Perth Amboy, N J —the fluosilicate bath was used Its composition was about 15 per cent hydrofluosilicic acid and 4 per cent tin, with sulfuric acid added as a lead precipitant The baths produced metal of 99 96 to 99 98 per cent tin content At the Perth Amboy plant the company made its own hydrofluosilicic acid in the sulfuric acid plant The cathodes in initial operation were enclosed in porous cells After the solution had taken up 6 per cent of tin, the porous cells were removed The voltage across the tanks was then changed from 4 to 5 volts to 0 5 volt Sulfuric acid was added as it was used up The porous cells used in the first part of the process were supported by glass blocks and by clips on rods from which the cathodes were suspended

The tin-refining plant at Perth Amboy in 1917 consisted of 68 tanks similar in size and construction to those used for copper The tanks were wood, lined with an asphalt coating The electrolyte was circulated from tank to tank through hard-rubber fittings Each tank in the

[9] *Trans Am Electrochem Soc*, **33** 155 168 (1918)

refinery contained about 11,000 pounds of anodes The cathode start-
ing sheets were of tin about ⅛ inch thick, made by casting in a
mannei similar to the making of thin lead cathode sheets The cuirent
density was about 12 amperes per square foot (1 2 amp /sq dm), the
metal deposition per ampere hour being about twice that of copper
(theoretically 2 2188 gr /amp hr Sn^{++}) The anode life was about 20
days and the output of the plant about 15 to 20 tons of tin metal per
day The product analyzed 99 96 to 99 98 per cent tin, which is purer
than the best Straits product The manufactuieis of high grade tin
foil, tin plate, and non-ferrous alloys reported the absence of manipu-
lative difficulties with this pure metal, which difficulties were always
more or less present with metal from Bolivian ores refined by pyro-
metallurgical methods

Mennicke, in his work on fluosilicate baths, obtained excellent de-
posits by the use of an electrolyte of 10 per cent tin and 10 per cent
hydrofluosilicic acid, operated at 20° C (68° F), with a current density
of 9 3 amperes per square foot (0 9 amp /sq dm) at 0 4 volt The
distance between his electrodes was 2 inches His electrolyte was made
by dissolving freshly precipitated stannous hydioxide in hydrofluosilicic
acid Free hydrofluosilicic acid was found not to interfere with satis-
factory deposition but the use of lead-containing cathodes caused spongy
deposits

While the fluosilicate bath functions in a satisfactory manner, it
has the disadvantage that it is difficult to prepare, it is none too stable,
and the materials used are expensive

Alexander and Stack, in an excellent paper on the "Reduction and
Refining of Tin in the United States," read before the American In-
stitute of Mining and Metallurgical Engineers in February, 1924,
described the operation of the Perth Amboy refinery in consideiable
detail Some of their statements follow

Tin is in a most desirable position in the electromotive series of the metals
for electrolytic refining The only impurity of frequent occurrence that stands
equal or close to tin and would dissolve is lead, all the others being below tin

Practically, lead is the only impurity that dissolves , consequently the electro-
lyte must contain a radical that will form an insoluble compound with lead, such
as a sulfate, chromate, fluoride, etc The other metals occurring as impurities in
tin (arsenic, antimony, bismuth, copper, etc) are not dissolved and remain in the
anode slimes

The requirements that a tin electrolyte should possess are (1) It must readily
dissolve tin from the anode and thus prevent the anode from becoming passive or
insoluble, with consequent high voltage and polarization , (2) it must be a good
conductor of electricity , (3) the cathode deposit must be adherent

Tin is a very crystalline metal and the cathode deposit from most electrolytes
consists of long dendritic or needle-like crystals These crystals are loosely attached
and grow rapidly, touching the anode causing short circuits The tin deposits for

satisfactory work should be smooth, dense, and adherent To obtain such a deposit from most tin electrolytes, an addition agent is necessary The electrolysis of tin had not been considered commercially practical by many metallurgists on account of these difficulties and the venture was undertaken with considerable apprehension

In the early part of 1915, Whitehead [8] investigated various electrolytes for tin refining, such as hydrochloric acid, sulfuric acid, hydrofluosilicic acid, hydrofluoboric, sodium stannate, sodium sulfostannate, etc After extensive experiments, hydrofluosilicic acid was selected as being the most satisfactory electrolyte

The electrolytes and addition agents that have been used are protected by a series of patents [10]

In their paper, referred to above, Alexander and Stack give the following description of the electrolytes used

The hydrofluosilicic acid bath was used from April, 1915, to October, 1917, and consisted essentially of fluosilicic acid with sufficient sulphuric acid to prevent lead from depositing by precipitating it as lead sulphate The approximate analysis of the electrolyte was

Specific gravity	1 20
Hydrofluosilicic acid	20 0%
Sulphuric acid	0 1%
Stannous tin	6 0%
Total acid in terms of H_2SiF_6	20 15%
Addition agent	glue

[10] Fluosilicate Bath patents United States 1,487,124, J R Stack In refining tin containing lead, contamination of electrolytically deposited tin is prevented by use of an electrolyte comprising a solution of tin in cresolsulfonic acids or other sulfonic acid together with a protective reagent as glue and cresylic acid and sulfuric acid which converts the lead in the dissolving anode into an insoluble compound

United States 1,487,125, J R Stack Specifies a process of refining tin bullion containing various other metals, as gold, silver, lead, copper, arsenic, antimony, and bismuth The electrolyte is of dilute hydrochloric acid or other reagent which will hold tin and bismuth in solution while other metals are deposited as slimes or precipitates Bismuth is precipitated, leaving the tin in solution

United States 1,397,222, F C Mathers Electrolytic refining of tin An electrolyte containing hydrofluosilicic acid, cresylic acid and less than 6 per cent tin is employed to produce an even continuous action without polarizing

United States 1,487,136, H H Alexander Electric current is passed from impure tin as an anode in an electrolyte of hydrofluosilicic with an excess of sulfuric acid to protect the bath from contamination by lead

United States 1,157,830, R L Whitehead Fluosilicate bath plus sulfuric acid to precipitate lead

Great Britain 183,507 (1921), A E White An agent such as one of the phenols or their homologs or benzene is added to an electrolyte containing H_2SiF_6 to obtain coherent deposits from a solution containing less than 6 per cent Sn Electrolyte may be prepared by passing current through an impure Sn anode and a solution containing 5 5 per cent H_2SiF_6, 5 per cent H_2SO_4, 0 3 per cent cresol, the impure commercial form of which is preferred A little glue may be added

Japan 42,643 (1922), Zenshichi Kimura The electrolyte contains fluosilicic acid 7 per cent, Sn fluosilicate 11 per cent, $SnSO_4$ 0 3 1 per cent, HF 0 02 per cent, glue 0 3 per cent, and beta naphthol 0 01 per cent Plain and even deposits of Sn above 99 9 per cent purity are easily obtained

Great Britain 220,012 (1923), American Smelting and Refining Co An electrolyte is used containing an organic sulfonic acid in sufficient amount to prevent the formation of basic Sn salts and to produce a dense smooth and adherent deposit Electrolyte may comprise Sn 4 per cent, H_2SO_4 5 per cent, hydrofluosilicic acid 2 per cent, and cresolsulfonic acid 2 per cent H_2SO_4 must be present in excess of the sulfonic acid to precipitate lead

Great Britain 240,147 (1924), J Neurath In refining Sn alloys containing lead, electrolyte is used which contains an anion such as SO_4 to reduce the concentration of lead ions and prevent cathodic separation of lead Copper and antimony may be deposited with the tin by use of "formers of complexes" such as NH_4 salts, or Sn content of deposit may be raised to 99 5 per cent by introducing S ions into the electrolyte

Great Britain 254,284, E A C Smith (1925) Tin bearing material is leached with a mixed

The deposit was only fair, not being dense, but sufficiently adherent to run 48-hour cathodes The anode corrosion caused considerable trouble, frequently occasioning high voltage with deposition of silica at the anode

One of the salient features of the process was the glue-cresylic acid addition agent, which was introduced in August, 1917 It was first used successfully in the tin-fluosilicate bath and later adopted in all other electrolytes used The addition agent commonly used is crude cresylic acid, added in the form of an emulsion with the glue Many other coal-tar products analogous to cresylic acid can be used as well The use of these reagents is due to F C Mathers [11]

The action of this addition agent produces a dense, smooth, adherent deposit of tin free from growths and frequently shows the vertical striations familiar in copper deposits Many theories have been advanced as to the action of addition agents, such as   (1) They act as a restraining agent to prevent the formation of a crystalline deposit (2) They migrate by the action of the current and form a film or envelope around the cathode, thus insuring even distribution of the current and preventing the formation of points of high current density (3) They form a compound with the metal from which the metal deposits (simultaneously with the metal from other compounds) in a smooth non-crystalline form or in compact blunt crystals When this form of crystallization has once been established, the metal subsequently deposited tends to follow the same form (4) The addition agent actually deposits at the cathode together with the metal, causing it to deposit in a non-crystalline form of fine blunt crystals

The theory that the addition agent deposits with tin has been found to be a fact in some instances In all tin electrolytes used, the addition agent becomes depleted at a constant given rate, varying from ⅓ to 3 pounds of glue and 8 to 16 pounds of cresylic acid per ton of tin refined, depending on the character of the electrolyte used Small fractions of a per cent of hydrochloric acid retard the action of the addition agent

The sulphuric-hydrofluosilicic electrolyte bath was used from October, 1917, to April, 1920, and consisted essentially of sulphuric acid with sufficient hydro-fluosilicic acid to prevent the formation of basic salts of tin The approximate analysis of the electrolyte is

Specific gravity	1 15
Sulphuric acid	8 0%
Hydrofluosilicic acid	5 0%
Stannous tin	3 0%
Total acid in terms of H_2SO_4	11 4%
Addition agent	glue and cresylic acid emulsion

The bath offered many advantages over the straight fluosilicate electrolyte The mastic-lined tanks, hard-rubber solution lines, bronze pumps, etc , were replaced with lead Better anode solubility and less decomposition of hydrofluosilicic acid during electrolysis were obtained

The sulphuric-sulphonic acid electrolyte was used from April, 1920, until the plant ceased operation (1923) A sulphonic acid was substituted for hydrofluo-silicic acid to prevent the formation of basic salts of tin, which occur when sulphuric acid is used alone and render the anode insoluble

The sulphonic acids can be made from benzol, phenol, cresol, toluene, naphtha-lene, and other aromatic hydrocarbons, by mixing with strong sulphuric acid and heating according to conventional methods for the manufacture of sulphonic acids If made, for example, from phenol, the new compound called phenol sulphonic acid is produced This is an avid solvent for tin and other metals forming a soluble salt with lead in contradistinction to sulphuric acid

If an electrolyte be made up containing 10 to 15% of either cresol or phenol sulphonic acid, 0 5 to 1% of sulphuric acid to prevent the deposition of lead,

solvent containing Sn and Fe compounds and acid, and the solution is electrolyzed to deposit a portion of the tin and regenerate the solvent
United States 1,452,573, L D Simpkins An electrolytic bath of a tin salt, *e g* , stannous sulfate, is formed with an admixture of a peptone or other colloid and beta-naphthol, which serve to facilitate production of dense, coherent deposits
[11] "Electrolytic Refining of Tin," U S Pat 1,397,222 (1921)

The tin-anode slimes adhere to and closely maintain the form of the anode so before the scrap anodes are removed the slimes are carefully scraped off filter pressed, washed, and sent to a department for treatment and recovery of the values Approximately 5% of slimes is produced per ton of tin refined, containing about 30 pounds of tin per ton of metal refined, or 98 5% of the tin is deposited from the anodes

A representative analysis of the anode slimes is Lead 20%, copper 5%, arsenic 3%, antimony 5%, tin 30%, bismuth 20%

Table 7 shows comparative analyses of electrolytic and other brands of tin The samples were taken at users' plants and the analyses were made by the Perth Amboy laboratory

TABLE 7

COMPARATIVE ANALYSES OF ELECTROLYTIC AND OTHER BRANDS OF TIN

	Pb per cent	Cu per cent	As per cent	Sb per cent	Bi per cent	Sn per cent	Total per cent
May, 1917, Electro-							
lytic	0 070	0 015	0 004	0 002	0 007	99 88	99 989
Penang	0 023	0 045	0 010	0 019	0 009	99 88	99 986
April, 1918, Electro-							
lytic	0 007	0 030	0 006	0 012	0 015	99 93	100 000
Penang	0 030	0 055	0 040	0 040	0 015	99 80	99 980
May, 1919, Electro-							
lytic	0 002	0 010	0 005	0 005	0 017	99 93	99 969
Banka	0 005	0 015	0 067	0 033	0 010	99 84	99 970
Straits	0 010	0 010	0 018	0 024	0 020	99 89	99 972
June, 1920, Electro-							
lytic	0 030	0 025	0 005	0 005	0 030	99 90	99 985
Straits	0 160	0 050	0 020	0 020	0 011	99 72	99 981
Dec, 1921, Electro-							
lytic	0 0025	0 020	0 003	0 004	0 015	99 94	99 985
Straits	0 055	0 070	0 030	0 030	0 029	99 77	99 984

This tabulation shows that the electrolytic tin is lower in the impurities lead, copper, arsenic and antimony and higher in tin than the foreign high-grade brands of tin

Electrolytic tin cannot be surpassed for uses that necessitate high-purity tin For some uses, such as tin plating, on account of its high purity it is necessary to add small percentages of impurities in order to produce the same effect as obtained with Straits or Banka tin It has been demonstrated that when the metal was too pure the desired thickness of coating would not be as readily produced as when limited amounts of impurities were present It is natural to suppose that certain ingredients would be more desirable than others, hence the high purity of electrolytic tin permits adjusting the composition of the metal to that found best for any particular use

SULFATE ELECTROLYTES [12]

In the search for baths less expensive than the fluosilicate, workers in the field turned to sulfuric acid as a source of a cheap ion It was shortly found that electrolytes such as sodium sulfate alone produced spongy non-coherent deposits, and that with sulfuric acid crystalline deposits were produced which soon short circuited the electrodes It is claimed that the cathode deposit can be modified in a satisfactory

[12] Schlotter, U S Pat 1,426,678, Norrie, Canada Pat 211,475, Schlotter, British Pat 148,334 (1920), Michaud and Delasson, Brit Pat 20,557 (1912)

manner by the use of addition agents such as gelatin, phenol, phloro-glucinol, or similar substances Later work by Schlotter showed the necessity of having the straight sulfate bath free from alkalies and ammonium salts One of Schlotter's baths has the following composition 120 grams stannous sulfate, 2 grams gelatin per liter Gelatin and cresylic acid soap emulsion as addition agents have temporarily produced satisfactory deposits of tin, but their activity seems to be quickly destroyed

Kern [18] tested solutions containing 5 per cent tin as (A) $SnCl_2$ $2NaCl$ with 2 per cent excess sodium chloride, (B) $Sn(BF_4)_2$ with 4 per cent excess HBF_4, (C) $Sn(SO_3 C_{10}H_7)_2$ with 8 per cent excess of $HSO_3C_{10}H_7$, (D) $SnSO_4$ with 2, 4, and 6 per cent excess of sulfuric acid The anodes were 95 per cent tin, 3 per cent bismuth, and 0 5 per cent each of lead, antimony, and silver The current density was 16 amperes per square foot, with electrode spacing 1 75 inch The tests were made at bath temperatures of 20 and 40° C It was concluded that (1) no smooth, adherent deposits are formed without addition agents, sulfate baths gave better deposits than the others, (2) 2 per cent excess sulfuric acid in sulfate baths was not sufficient to make the solution remain clear, (3) peptone and gelatin, 1 to 2 grams per liter, improved deposits, effectiveness of addition agents is increased by rise in temperature, (4) current efficiencies are high only when the deposit is smooth, dense, and adherent

The sulfuric-acid bath becomes inoperative in the case of anodes containing appreciable amounts of lead, say 2 per cent or thereabouts This is a decided disadvantage in using this bath for commercial tin metal produced from Bolivian ores

When sulfuric acid and sodium sulfate are used together as an electrolyte, the tendency of the acid to cause crystalline deposits is neutralized by the tendency of the sulfate to form sponge metal By properly balancing the proportions of one constituent against the other, a coherent, dense, cathode deposit, satisfactory for commercial refining, is produced

A bath which has proved satisfactory for commercial tin refining at the present time is that of Fink [14] which has about the following composition 233 grams Na_2SO_4 $10H_2O$, 150 grams H_2SO_4, 35 grams Sn, 2 grams aloin per liter, which, in the case of high lead content anodes, is modified to the following: 60 to 120 grams Na_2SO_4, 50 grams H_2SO_4, 35 grams Sn, 2 grams aloin The Glauber's salts may be replaced by

[18] *Trans Am Electrochem Soc*, 38 143 162 (1920)
[14] C G Fink, U S Pat 1,466,126

salts such as ferrous sulfate without greatly impairing the cathode deposit, yet improving the anode corrosion

This bath has the advantage that high lead content anodes can be refined, the electrolyte is inexpensive, thick deposits can be obtained without treeing, the bath is operative satisfactorily at room temperature and no heating is required, no diaphragms are necessary, the impurities in the anode form an easily removed sludge, and circulation with no bad effects but only the desired good ones is possible and made use of. The addition agent, aloin, is cheap, easily prepared, and remains active for a relatively long period of time. There is present in the bath a prepondering concentration of sulfate ions, and small amounts of chloride, fluoride, or fluosilicate ions may be present and not be prejudicial to the final result. In addition the electrolyte contains a prepondering concentration of ions more electropositive than tin, such as sodium, and as a result of the refining, magnesium, iron, aluminum, chromium, etc., which will not be deposited in preference to tin because of their more electropositive nature

The commercial current density is 10 amperes per square foot, the voltage being 0 2 or less. With reduced acid concentration the voltage may rise higher

Additional metal sulfates such as those of iron, titanium, cobalt, nickel, manganese, and chromium when added to the tin refining cell have the beneficial effects of loosening the slimes which tend to adhere to the anode, thus rendering anode corrosion easier, and of improving the density, hardness, and blend of crystals deposited on the cathode

The alkaline sulfide baths for refining are unstable, will not permit circulation, and have to be externally heated, the same holds true for the alkaline baths which have the additional disadvantage that anode corrosion is greater than cathode deposition. The organic acid baths are unstable and expensive, useful only for electroplating, the same holds true for the boric and phosphoric acid baths. Tin is deposited from neutral or alkaline baths in a finely granular or spongy condition, which deposits are difficult and expensive to handle. Acid baths give rise to "tree" deposits which eventually short circuit the electrodes. Acid baths containing chlorides give rise to very long crystals. Certain organic addition agents used in this bath will reduce the size of the cathode crystals, but large quantities of addition agents are required to produce deposits easily handled without mechanical loss. A similar set of conditions holds true for the sulfuric acid bath. The fluosilicate bath, while producing satisfactory results, is expensive and needs the addition of sulfuric acid to prevent the deposition of lead along with

the tin The sulfate bath (such as sodium sulfate or stannous sulfate) tends to give spongy deposits of the same character as those from alkaline or neutral baths The combination sulfuric acid—alkaline sulfate—tin sulfate bath combines the treeing of the acid bath with the sponge deposit of the alkaline bath by neutralization of one effect by the other, producing a satisfactory medium for commercial electrolytic tin refining The combination sulfuric acid-sulfonic acid bath has satisfactorily operated over a number of years producing the highest grades of tin known It meets all the necessary conditions for commercial refining Being on a sulfuric acid base it is relatively inexpensive It can be readily controlled and entails no unusual and not fully tested materials of construction

CHAPTER 9

PLATING

The electrodeposition of tin is of considerable importance in industry There seems to be, however, a number of misconceptions in respect to the subject Just as nickel plating is supposed by some to prevent corrosion or rusting when applied to iron and steel, so is tin plating Altpeter[1] maintains that zinc serves both to protect and improve the appearance of the iron and steel upon which it is applied, but that tin serves only the latter decorative purpose This view is too extreme, for tin will certainly protect the base metal to some extent It affords protection, however, only when it completely covers the base metal upon which it is deposited Inasmuch as tin solutions are usually better conductors than nickel-plating baths with higher throwing powers, the covering of tin over iron and steel is much more nearly continuous than that of nickel Thus there are fewer points or pinholes available for corrosion attack Tin, like lead and nickel, has no inherent property to cause it to protect iron, to which it is electro-negative It will thus protect only where it completely covers Tin is more resistant to fumes and the atmosphere than is zinc, but it is ordinarily less resistant to gaseous attack than lead or nickel

The possible uses and applications of tin plating are not so widely known as they deserve to be Tin plating finds large application as a covering for copper and steel in cooking kettles for food products, iron and steel containers, refrigerator coils in machines of the electric type and in a large number of cases where decorative coverings are desired Electro-tinning is used to deposit tin on such classes of goods as lighting fixtures, ornamental hardware, buckles, and a large number of metal objects Often it is desired to deposit a coating on the iron, brass or other base metal which is cheaper than silver and yet can be "oxidized" or "colored" Some very beautiful effects can be produced by this method Close inspection is required to distinguish the "finish" from that of oxidized silver Tin has an advantage over silver in this application in that if the protective lacquer should wear off, the tin is

[1] *Stahl Eisen*, 36 780 (1916)

not so readily tarnished as silver would be An interesting use of tin plating is the application of exceedingly thin deposits on white gold jewelry to bring up the "color" and uniformity of appearance

Electrolytically deposited tin is of a dull or matte white color It has so far not been possible to deposit tin so that it might be removed from the bath in a bright condition Ordinarily it is necessary to scratch-brush the deposit and further polish it if it be desired to produce the same bright surface as is made when the base metal is coated by hot dipping This disadvantage has often prevented the adoption of the electrolytic method for tin coating Electro-deposited tin is soft, malleable, and very ductile With continued deposition, the deposits tend to become more and more crystalline The deposit is apt to become spongy, slimy, or dendritic, with little adherence The addition of colloids to the bath allows the production of thicker deposits These retain the ductility and characteristic softness of the metal.

The number of tin-plating baths recommended in text books, journal articles, and patent specifications has been very large Few of them have wide application and many are worthless At the present time the alkaline tin baths, modified in a large number of ways, are practically the only ones which are commercially important They will serve for almost any purpose to which tin plating may be applied Ordinarily, the required thickness of a tin deposit does not exceed a fraction of a mill (0 001 inch) These deposits are usually smooth and apparently without definite structure In their formation they have not had time to appear crystalline to the eye nor develop trees In a number of cases, comparatively thick deposits are required An example is the coating of copper sheets for fabrication into equipment for the dairy and food industries where deposits 0 003 inch thick of an absolutely continuous nature are required Refrigerator coils also need thick deposits The acid tin baths proposed from time to time have lacked the necessary throwing power A common commercial alkaline bath is. sodium stannate 28 ounces per gallon (210 grams/liter), hydrated stannic oxide 2 ounces per gallon (15 grams/liter), powdered white starch ⅛ ounce per gallon (0 9 gram/liter) Potassium resinate is used as a colloidal addition agent, being added as required to improve the character of the deposit The bath is operated at a temperature of 160° to 180° F (71 11° to 82 22° C) with a current density of 25 to 40 amperes per square foot (2 5 to 4 amps /sq dm) at 4 to 6 volts Thirty per cent of sheet steel anodes are used and 70 per cent of tin The anode efficiency is about 60 per cent of that at the cathode Sodium stannate and hydrated tin oxide are added at intervals to maintain the solution Small amounts

of chlorides are advantageous Hughes [2] gives an English bath compo-
sition of ½ pound of caustic soda per gallon (60 grams/liter), and
1 pound of stannous chloride crystals (120 grams/liter), with the addi-
tion of 1 ounce of potassium cyanide per gallon (7 5 grams/liter) Blum
and Hogaboom [3] give a bath composition successfully applied during
the war stannous chloride crystals 4 ounces per gallon (30 grams/liter),
sodium hydroxide 10 ounces per gallon (75 grams/liter), glucose 8
ounces per gallon (60 grams/liter), operating at 50° C (122° F), at a
current density of 9 amperes per square foot (1 amp /sq dm) They
state that the dextrin or analogous material is a very essential and effi-
cient addition agent in these baths Almost every text book, however, has
its own proportions [4] Practical experience shows that considerable
variation is allowable The stannous chloride or the sodium stannite
or stannate contains the metal to be deposited The caustic alkali
acts as a conducting salt and helps to dissolve tin from the anodes
The cyanide, if it be added, aids anode corrosion, keeping them clean
and free from slime Knox [5] states that with current densities of 10
amperes per square foot (1 amp /sq dm) of cathode surface, plating
efficiencies run 40 to 60 per cent or higher in some cases Mathers
and Bell [6] investigated alkaline stannite baths to determine whether
they could produce a commercially useful and adherent deposit by the
action of addition agents such as gum sandarac, rosin, glue, oleic
acid, gum tragacanth, manna, aloin, sodium sulfide, and balsam copaiba
Only the last was found suitable and rosin ranked next The bath con-
tained crystalline stannous chloride 60 grams per liter (8 oz /gal),
sodium hydroxide 60 grams per liter (8 oz /gal), and addition agent
1 gram The current density was 4 7 amperes per square foot (0 47
amp /sq dm) Cast-iron anodes showed only 76 to 78 per cent cor-
rosion, while amalgamated refined tin gave 100 per cent efficiency
Temperatures of 75° to 90° C (167 to 194° F) gave deposits superior
to those at 50° C (122° F) Continued satisfactory deposits could not
be obtained, due to gradual oxidation of the sodium stannite No method
of prevention or regeneration was found

One of the oldest alkaline baths is that of Beneker, consisting of
sodium hydroxide 125 grams per liter (16 6 oz /gal), stannous chlo-
ride 50 grams per liter (6 6 oz /gal), and sodium thiosulfate 75 grams

[2] *Beama* 10 138 41 (1922)
[3] "Principles of Electroplating and Electroforming," New York, McGraw Hill Book Com
pany, Inc , 1924
[4] Stockmeier, "Handb d Galvanostegie," Halle, W Knapp, 1899, p 116, Langbein, Brannt,
"Electrodeposition of Metals," Philadelphia, H C Baird & Co , Pfanhauser, "Galvanotecknik,"
Berlin, J Springer, 1910, p 601
[5] *Metal Ind* , 18 361 2 (1920)
[6] *Trans Am Electrochem Soc* , 38 135 42 (1920)

per liter (10 oz /gal) A large amount of experimental work has been done to improve the alkaline baths Mantell developed a bath particularly applicable for plating on copper to produce heavy deposits of a highly protective nature This bath is decidedly alkaline with all the desirable characteristics of the alkaline baths, none of the bad ones, and all of the desirable characteristics of the fluoborate acid bath When made from sodium stannite the composition is sodium stannite 10 grams per liter (1 33 oz /gal), borax 1 gram per liter (0 13 oz /gal), sodium fluoride 4 grams per liter (0 53 oz /gal), sodium hydroxide 2 grams per liter (0 26 oz /gal) When made from sodium stannate (a commercial salt containing 50 to 60 per cent tin, a by-product resulting from the detinning of tin plate scrap by the caustic electrolytic process) the bath is sodium stannate 12 grams per liter (1 6 oz /gal), borax 1 gram per liter (0 13 oz /gal), sodium fluoride 4 grams per liter (0 53 oz /gal), caustic 2 grams per liter (0 26 oz /gal). The deposit of tin is very white, exceedingly fine-grained, and very readily polishable The bath has very good throwing powers In operation it should be practically free from chlorides and sulfates At current densities of 12 to 20 amperes per square foot (1 2 to 2 amp /sq dm), at temperatures from 170° F (76 7° C) up to the boiling point, and at voltages of 4 to 6 volts, no difficulty is met in obtaining tin deposits as thick as 0 008 to 0 010 of an inch The Roessler and Hasslacher Chemical Company has recently developed an alkaline sodium stannate-acetate tin bath of the following composition sodium stannate 12 ounces per gallon (90 grams/liter), sodium acetate 2 ounces per gallon (15 grams/liter), sodium hydroxide 2 ounces per gallon (15 grams/liter), hydrogen peroxide (25 vol) one-fifteenth ounce per gallon (0 5 gram/liter) Excellent deposits of tin on steel, copper, brass, lead, zinc, cast iron, and zinc die castings have been obtained in barrel plating at current densities of 10 to 15 amperes per square foot (1 to 1 5 amperes/sq dm) with solution temperatures of 70 to 80° C (158 to 176° F), at 6 to 8 volts This bath will deposit 0 15 to 0 20 ounce per square foot (0 00024 to 0 00032 inch thickness) of tin per hour at the above current densities In still plating, current densities may be increased to 20 to 60 amperes per square foot (2 to 6 amps /sq dm) and thicknesses of smooth, white tin deposits up to one-quarter of an inch may be produced Under the best operating conditions, anode and cathode current efficiencies when based on tetravalent tin are from 85 to 95 per cent When steel anodes are used with the tin anodes, the efficiency of the tin anodes markedly decreases As a safeguard against sponging and discoloration of deposits, small amounts of hydrogen peroxide are added

simultaneously with each addition of caustic made when the caustic content is too low If the caustic content be too high, small amounts of acetic acid must be added to reduce it Each addition of acetic acid must be followed immediately by the addition of small amounts of hydrogen peroxide

The simplicity of the alkaline tin bath is more apparent than real In operation, the composition of the solution will become more complicated, due to adsorption of oxygen and carbon dioxide of the air and the electrode reactions resulting from electrolysis Tin is found to dissolve anodically in the tetravalent form, giving the stannate This, when coupled with the fact that alkaline stannite solutions decomposed spontaneously giving metallic tin and stannate, led to the belief that the relations between stannic and stannous ions and metallic tin were such that the equilibrium of the equation $2Sn^3 \rightleftarrows Sn^4 + Sn^\circ$ was very much in favor of the right-hand side In acid solutions, however, tin dissolves anodically as stannous ions Goldschmidt and Eckardt [7] found that pure tin readily became passive It dissolves in alkaline solution in the stannous condition Foerster and Dolch [8] found that tin to stannous ion and not tin to stannic ion is the stable system They state that colloidal tin compounds are precipitated on the electrode at certain concentrations These prevent the diffusion of the stannous or stannite ion away from the anode, with the result that the anode potential is raised to the value necessary for oxygen evolution The tin is thus passivated The stannite is rapidly oxidized to stannate This film action is catalyzed by insoluble impurities present in the tin The lower the current density and with higher temperatures, the more tin can be dissolved before the formation of stannate occurs If the electrode be scraped, it again becomes active The chemical precipitation of tin from alkaline stannite solution is preceded by a great diminution of the stannate-ion concentration, due to a gradual formation of non-ionized colloidal metastannic acid

In addition to the present satisfactory alkaline baths, there are a number of more or less useful baths of different composition Hollard [9] states that spongy deposits were prevented by the use of an electrolyte of sodium stannite 12 grams per liter (1 6 oz /gal) and sodium sulfate 200 grams per liter (26 6 oz /gal), operated at a current density of 2 amperes per square foot (0 2 amps /sq dm), at a temperature of 80° C (176° F) Mathers and Cockrum [10] found that the various

[7] *Z physik Chem*, 56 385 (1906)
[8] *Z Electrochem* 16 599 (1910)
[9] *Bull soc enc ind nat*, July, 1912, p 28
[10] *Trans Am Electrochem Soc*, 29 405 10 (1916)

baths for tin plating described by Kern [11] did not in any case produce an entirely satisfactory deposit when operated under the conditions recommended They obtained smooth, firm deposits with the Beneker bath but considered it far below the quality desired for electroplating They found that the addition of peptone to a modification of Kern's stannous ammonium oxalate bath containing 2 to 3 per cent stannous chloride, 5 5 to 6 5 per cent ammonium oxalate, and 0 3 to 0 4 per cent of oxalic acid gave a smooth, firm, and finely crystalline deposit which was the best obtained from any bath As a result of further study,[12] they recommended a most satisfactory bath to be 5 per cent stannous oxalate, 6 per cent ammonium oxalate, 1 5 per cent oxalic acid, and 0 25 per cent peptone It is run at room temperature at 0 4 amperes per square decimeter (4 amps /sq ft), with frequent stirring Additional peptone is added when the deposit shows projecting crystals There is no doubt that the addition agents are deposited along with the metal, for they are always found in the cathode after it is taken from the bath

Quintaine [13] claimed that he could obtain a perfect deposit of tin from either stannous or stannic chloride with the addition of a salt such as ammonium chloride There has been no commercial application of this bath Lottermoser and Brehm [14] found that a good deposit of tin can be obtained from a pyrophosphate bath, without further additions, at a temperature of 50° to 60° C (122° to 140° F) The composition of the bath is as follows fused stannous chloride 16 grams per liter (2 13 oz /gal), stannous chloride crystals 4 grams per liter (0 53 oz /gal), sodium pyrophosphate 50 grams per liter (6 7 oz /gal) The best results are obtained if 5 to 6 grams of tartaric acid be added to the above bath This changes the pH from 3 44 to 1 7 The addition of a colloid is unnecessary The cathodic current density should not exceed 0 02 ampere per square decimeter

Battle [15] has patented an electrolyte for tin plating containing phosphoric acid, a tin salt such as the chloride or sulfate, and sodium pyrophosphate with the addition of colloids such as gelatin and gums A phosphate bath first proposed by Roseleur is employed commercially It has the following composition· stannous chloride crystals 1 ounce per gallon (7 5 grams/liter), sodium pyrophosphate 8 ounces per gallon (60 grams/liter), dextrin 1 ounce per gallon (7 5 grams/liter), operated at a temperature of about 60° C (140° F) at 5 amperes per square

[11] *Trans Am Electrochem Soc* 23 199 (1913)
[12] *Trans Am Electrochem Soc* 29 411 4 (1916)
[13] British Pat 5,496 (1900)
[14] *Z Elektrochem* 27 573-9 (1921)
[15] U S Pat 1,202,149 (1917)

foot (0 5 amp/sq dm) Marino[16] has patented a tartrate bath for the deposition of tin, as well as various phosphate baths containing sulfanilic acid

A German bath[17] employed to deposit surfaces to resist etching and employed in galvanoplasty is made up in the following manner 2 kg (266 6 oz) sodium pyrophosphate in 10 liters (2 63 gals) boiling water, 2 kg (266 6 oz) stannous chloride added gradually The resulting precipitate is washed with water, dissolved in 10 liters (2 63 gals) of water and 2 kg (266 6 oz) sodium pyrophosphate, the solution made up to 100 liters (26 3 gals), and 200 grams (26 6 oz) dextrin in water, 250 grams (33 3 oz) tartaric acid, and 600 grams (80 oz) sodium chloride added Mathers[18] has patented an electrolyte for tin plating consisting of stannous sulfate saturated with cresylic acid to improve the smoothness of the tin coating Schlotter[19] states that dense adherent deposits are obtained from acid tin salt solutions containing a colloidal substance and free from alkalies and ammonia A suitable solution contains stannous sulfate 120 grams per liter (16 oz /gal), and gelatin 2 grams per liter (0 26 oz /gal) Such solutions are suitable for depositing on copper, brass, or the like For plating iron galvanos prior to backing them with molten-lead alloy, it is necessary, however, to employ an addition agent such as phenol or phloroglucinol The electrolyte may then consist of stannic chloride 150 grams (20 oz), gelatin 2 grams (0 26 oz), phenol 5 grams (0 66 oz), hydrochloric acid 5 grams (0 66 oz), and 1 liter (0 26 gals) of water Schlotter[20] has patented a tin-plating bath containing stannous sulfate with the addition of gelatin, phloroglucinol, or a similar substance to the solution before electrolysis

It will be noted that in practically all of the successful tin-plating baths there is low ionic tin concentration obtained either as a result of dilute solutions or of the formation of complex ions Many of the older alkaline baths had the defect that the solutions deteriorated on standing No method for eliminating this deterioration has been found There still remains a broad field for work to be done in connection with tin-plating baths, inasmuch as no entirely satisfactory bath has been found that will give good, smooth, and thick deposits of tin over very long periods of time No tin baths are known which will give bright tin deposits directly from the solution so that polishing would not be necessary One great fault of tin-plating baths is that anode

[16] British Pat 11,011 (1915)
[17] German Pat 270,181, April 26, 1912
[18] U S Pat 1,540,354 (1925)
[19] British Pat 148,334 (1920)
[20] U S Pat 1,424,678

corrosion is not so good or efficient as is desired There has been very much less research work done on tin anodes than on nickel

Deposition of tin alloys, particularly those of lead and tin, from fluoborate solutions has been carried out successfully by the United States Navy Department in recent years, particularly for liners in torpedo flasks and similar objects Blum and Haring [21] found that lead and tin have nearly equal potentials in fluoborate solutions They will displace each other depending upon their respective metal ion concentrations Solutions which are of 1 *N* metal and 0 5 *N* free hydrofluoboric acid concentrations, when agitated with tin or lead, reach equilibrium at about 0 81 *N* tin and 0 19 *N* lead, because then the two metals have the same potential This equilibrium is not affected by glue but is appreciably influenced by the acidity and total metal concentration Cathode efficiencies under normal conditions are nearly 100 per cent, and the metal deposits obtained depend upon the metal ratio in the solution Current densities of 0 5 to 1 5 amperes per square decimeter (4 7 to 14 amps /sq ft) are employed with lead-tin anodes containing somewhat less tin than is desired in the deposits Feith [22] has patented the addition of small amounts of cadmium, preferably in the form of cadmium chloride, to the amount of 30 to 60 grams (4 to 8 oz), to tin salt 1 to 2 kg (133 3 to 266 6 oz) in 100 liters (26 gals) of solution as an electrolytic tinning bath It is believed that the future will bring much more extensive applications of electrolytic tinning, particularly for the deposition of tin alloys of the tin-lead, tin-cadmium, tin-bismuth, and tin-antimony type

NON-ELECTROLYTIC METHODS OF TIN PLATING

Large quantities of small articles such as pins, thimbles, eyelets, dress snap fasteners, chain links, safety pins, buttons and the like, are coated with tin by the contact process This method is an immersion one, and strictly speaking is not electrolytic The current, instead of being furnished from an outside source, arises in the tank itself This method is applied largely for decorative purposes The coatings are very thin but very fine-grained and bright Unlike most deposits produced by immersion, they are decidedly adherent, with considerable resistance to corrosion The ionic concentration of tin in the baths is very low, hence the rate of deposition is slow and treeing is effectively prevented Hydrogen has a relatively high overvoltage on tin, this aids in the production of dense impervious deposits All of the immersion

[21] *Trans Am Electrochem Soc ,* 40 147 (1921)
[22] German Pat 205,051 (1907)

processes depend upon the electrolytic action of the base metal—i e, the metal being plated) Deposition thus necessarily stops as soon as the base metal is entirely covered It is thus possible to secure only very thin deposits

One of the most common solutions for tinning by immersion is prepared by making a saturated solution of cream of tartar ($KHC_4H_4O_6$) in water, adding about $\frac{1}{2}$ ounce of stannous chloride to each gallon (3 75 grams per liter), and raising to the boiling point The articles to be treated are contained in a tin sieve or the solution is placed in a strong solid tin vessel and the articles agitated with a tin rod

Another simple bath is that proposed by Elsner, used for copper or brass goods It consists of $\frac{1}{4}$ of an ounce of sodium chloride and $\frac{1}{4}$ of an ounce of stannous chloride per gallon of water (or 1 8 grams of each per liter) Heated solutions are used

Where a better class of deposit is required, immersion tinning in the above or similar baths is done by having the articles in contact with pieces of zinc A quicker action ensues owing to electrochemical effect Stronger and more durable deposits result

Brass articles to be tinned are rotated for 2 to 4 hours at 80° C (176° F) in a barrel containing the solution and small pieces of zinc A widely used solution is stannous chloride crystals 3 ounces per gallon (25 grams/liter), and potassium acid tartrate ($KHC_4H_4O_6$) 1 3 ounces per gallon (10 grams/liter) When the pieces of brass and zinc come in contact in such a solution, a cell is formed in which the zinc is anode and the brass is cathode and becomes coated with tin The zinc passes into the solution, displacing the tin The acid tartrate causes the formation of complex ions to some extent This produces a small concentration of stannous ions The complex ions do not readily hydrolyze or precipitate tin hydroxides   .

The "cream of tartar" immersion process is somewhat similar to the above, the solution consisting of potassium acid tartrate 0 2 ounce per gallon (1 5 grams/liter) and sodium chloride 0 4 ounce per gallon (3 0 grams/liter) The brass articles are placed in thin layers on iron wire trays, covered with perforated sheets of pure tin and heated to at least 90° C (194° F) by steam coils in a copper tank for 3 to 5 hours The tin gradually passes into solution It never reaches a high concentration, for it is speedily plated out on the brass, the potential of which is similar to that of copper, i e , below that of tin in the electrochemical series Each batch of work requires a freshly made solution After coating, the work is rapidly rinsed and dried

Alkaline solutions are also employed for tin coating of brass by

immersion A typical solution contains stannous chloride crystals 4 ounces per gallon (30 grams/liter) and sodium hydroxide 8 ounces per gallon (60 grams/liter) The brass objects are placed in an iron vessel on iron wire trays, covered with perforated sheets of tin The vessel and its contents are heated to 90° C (194° F) for 2 to 3 hours Tin becomes the anode, passes into solution, and is deposited on the brass Solutions more dilute than given in the formula are used for very small articles

Iron articles are tinned by placement in thin layers on iron wire screen trays, covered with perforated zinc sheets in a galvanized iron tank The solution is heated nearly to boiling, the articles immersed and kept there for about three-quarters of an hour The heating of the solution is stopped when the articles are immersed A typical solution contains stannous chloride crystals 0 3 ounce per gallon (2 5 grams/liter), ammonium alum ($(NH_4)_2SO_4Al_2(SO_4)_324H_2O$) 0 25 ounce per gallon (2 0 grams/liter), and cream of tartar ($KHC_4H_4O_6$) 0 01 ounce per gallon (0 08 grams/liter) Usually the salts are dissolved in one-third the total quantity of water and then added to the other two-thirds of the water previously placed in the iron tank in which plating is to be done About one drop of sulfuric acid per gallon of solution is then added After the articles have been tinned, the solution is discarded and the articles quickly rinsed and dried

Articles for simple immersion tinning must be thoroughly and systematically cleaned After treatment in the tinning bath they are generally dried and polished by shaking in sawdust, leather scraps, whiting, or other polishing agents in tumbling barrels

CHAPTER 10

ALLOYS

The history of tin and its use in industry, its application to the arts, shows that it has been notable for its most profound effect on the physical properties of other metals It is very likely that one of the earliest observations of this manner was that tin would harden copper The modifying influence of tin on copper and lead has constituted one of the most useful if not the most important of all the properties possessed by the metal

Until the last decade, workers in metal were generally content to add one metal to the other Alloy making was largely based on their own past experience and the practices of others Scientific research work of the type which has resulted in our thermal equilibrium diagrams and our vastly increasing knowledge of metallic alloys is a product of the present generation As a result, the very numerous tin alloys have been the subject of much investigation, some for purely scientific purposes, but most of it with their industrial applications in view

An attempt has been made in this volume to gather together the most modern and accurate data, critically studied, on the subject of tin and its alloys

The commercial alloys of tin may, in general, be divided into two large classes first, the alloys with copper, commonly termed the bronzes, of which there are many variations, especially in the ternary and quaternary systems , and secondly, the so-called white metals, which are the alloys with antimony, lead, sometimes bismuth, and often with small proportions of copper The white metals are generally subdivided into the anti-friction or bearing metals, printers' alloys, the pewters and Britannia metal, the solders, and those special alloys applicable for special castings in the chemical industries, battery plates, bullets, collapsible tubes, and foil In addition to these, the so-called die-casting alloys and toy and mold metals are becoming increasingly important

BRONZES

It is probable that at first it was not metallic tin which was added to copper in the empirical work done for fitting copper for continual

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use in the edges of knives, axes, swords, and other tools of the same type It is more likely that the oxidized tin ores, together with some reducing agent, constituted the material added to the molten copper It was early found that tin had the power of hardening copper in a most remarkable manner Even to this day, the phenomenon has not ceased to be a matter of wonder Both the red-colored copper and the white tin are themselves soft The resulting bronze, when the two metals are alloyed in the proportion of 2 copper 1 tin, is a purer white than the white tin and as brittle as glass The ancients attributed the influence of tin to the devil Tin was called *diabolus metallorum,* which can be interpreted either the "devil of the metals" or else the "metal of the devil "

Bronzes, estimated to belong to the period of about 3500 B C , have been found upon analysis to have approximately the same proportion of copper and tin as the gun metal which was used for ordnance in all the European countries up to the time of the appearance of the modern steel artillery rifle Some of the bronzes of the Roman period contained lead in addition Bronzes of considerable antiquity have been found in the relics of some of the most ancient civilizations

One of the best known bronzes is gun metal, consisting of copper with 8 to 14 per cent tin, although the usual proportion in the alloys employed in ordnance is 90 10 One of its close relatives is Admiralty gun metal, containing 88 per cent copper, 10 per cent tin, and 2 per cent zinc The Admiralty alloy is accepted throughout the world as being a metal of widely varying application Another bronze of historical importance and application in the arts is bell metal, containing 15 to 25 per cent tin

The colors of bronzes are deeper and more attractive than brass in the polished condition, and they are markedly more resistant to corrosion In general the addition of tin to alloys or to other metals increases their corrosion resistance

Statuary bronzes have been much discussed in the literature, and the patinas or surface corrosion crusts have been the subject of much study Surface finishes, impossible of attainment from other alloys, add considerable beauty to works of art in enduring bronze

The scientific side of bronze alloys is discussed in connection with the tin-copper system elsewhere in this volume

Zinc is often added to bronzes because it is thought that the addition makes the molten alloy more fluid There is little doubt, however, that the addition of zinc decreases the corrosion resistance, particularly when the metal is exposed to the atmospheres of industrial centers

Many of the coveted honors in life are perpetuated in bronze An example is the Victoria Cross, the highest military decoration of the British Empire These were struck from gun metal taken from the trophies of the previous wars

Coinage metal of many countries, notable among which are England and France, is a bronze containing 95 per cent copper, 4 per cent tin, and 1 per cent zinc

The bronze alloys used in bell metal ordinarily contain metals other than tin and copper only in small traces if at all The bell metal is a hard and somewhat brittle alloy The purity of the tone of the bell is dependent upon the design and the accuracy of founding rather than composition, although the tone of the bell is modified by the proportion of copper and tin Bell metal is susceptible to heat treatment. When heated to redness and chilled, it is more malleable and of a more yellow color than is obtained when it is slowly cooled

In recent years, there has been developed a large number of special bronzes adapted to severe strains, high pressures, unusual engineering applications, and for places where other materials are unsuitable A number of these are listed elsewhere in this chapter under their special names, and their compositions given In recent years, the heat treatment of bronzes has been the subject of much study Our technical literature is now rich in this topic

Phosphor bronze has been one of the principal developments of the tin-copper alloys It is thought that the alloy had its origin as the result of an attempt to deoxidize the molten metal by the addition of phosphorus Phosphor bronze may then be considered as a greatly improved gun metal It is stronger and harder, and has markedly superior corrosion resistance The increased hardness is thought to be due to the microscopic crystals of copper-phosphorus and tin-phosphorus compounds embedded in the softer matrix of the alloy The material is used for making tubes, wire ropes, springs, screws, pinions, valves, steam fittings, pumps, axle bearings, cog wheels, parts of machinery exposed to great friction and stresses, as well as ornamental castings The proportion of phosphorus rarely exceeds 1 per cent, and above 4 per cent the alloy is considered to be useless The addition of lead is found to be markedly beneficial when the metal is used for bearings The alloy then becomes slightly plastic Increases of temperature have little effect upon the mechanical properties of phosphor bronze This is in marked contrast to the brasses, whose physical properties are greatly impaired by rise in temperature

WHITE METALS

The attention which the white metals have received from investigators has been small as compared to the bronzes Often the manufacture of the white alloys has been regarded among the so-called trade secrets Certain it is that the skill and experience of those engaged in preparing the metals are quite important Gun metals and phosphor bronzes have been displaced as bearing metals by the highest-grade white anti-friction metals, which have tin as a chief constituent Because of the high price of the tin metal, these alloys are generally quite expensive

It is generally held that a homogeneous alloy is not suitable for a bearing Thus neither a single metal nor a solid solution alloy can be employed with success The necessary surface for a bearing is obtained by a metal consisting of a soft matrix with hard crystals embedded in it, or of a hard metal interspersed with veins of a softer constituent The mottled surface resulting, in which the harder portions are in slight relief, provides a number of pools and canals to retain the oil film and promote the spreading of the oil over the surface of the bearing An alloy of approximately 93 per cent tin, 3 5 per cent antimony, 3 5 per cent copper is representative of the type favored for the big end bearings of aircraft engines It is thought to be one of the best bearing metals produced for strenuous and critical service Tin is capable of dissolving a considerable amount of antimony in the molten state, and retaining about 7 per cent in solution on solidification In this particular alloy, the cubical crystals ordinarily seen in tin-antimony alloys containing considerable antimony are not in evidence The copper forms hard compounds with tin, partially separates on cooling, and develops a network of fine needle-shaped crystals These are hard and remain embedded in the tough and hardened tin-base matrix This matrix gives the alloy the power to resist shock and bending stresses, as well as the destructive forces of constant and rapid vibration

As an example of a cheaper alloy of lower tin content, a representative analysis would show approximately 86 per cent tin, 10 5 per cent antimony, 3 5 per cent copper The antifriction properties are not quite equal to the alloys of higher tin content In the process of cooling, this alloy first deposits rich tin-copper crystals, and at a lower temperature cubical crystals of the tin-antimony compounds deposit These become enmeshed in the already formed but still soft copper-tin compound Finally the matrix solidifies and examination shows the two relatively hard materials embedded in the softer matrix The size and distribu-

tion of the crystals are greatly affected by the rate of cooling, which is carefully controlled in the manufacture of bearings using these alloys

The original patented Babbitt metal was a very high tin content alloy It was prepared in a special manner The somewhat mysterious method of metal mixing was the basis of the patent, inasmuch as simple alloys are difficult to protect The number of so-called Babbitt metals are legion, many of which are given in the table of alloys

In the case of most tin alloys, fractional solidification is always present This phenomenon is recognized by metallurgists, but not as often as it should be by workmen engaged in preparing the metals For this reason the chief benefits and the correct use of the alloys are often lost In many shops when the metal is cooled in the ladle, little regard is paid to temperature conditions The alloy is sometimes poured too hot and then allowed to cool Often, near the end of the operation, pouring is continued when a partial solidification has taken place in the ladle The still fluid metal is then allowed to run off from the semi-solid residue A little study of the thermal equilibrium diagrams will show that the two portions are not of the same composition, the semi-solid residue being much richer in copper and antimony Thus a series of bearings may be found to be of varying condition, even when poured from the same ladle, as the result of careless control of temperature conditions

The printing craft is dependent upon a series of white metal alloys, ordinarily of the ternary type The alloy generally used for cast type which the printer sets by hand was 5 to 20 per cent tin, 25 to 30 per cent antimony, and the balance lead In the earlier days of printing, larger amounts of tin were used, but cost considerations have caused a general effort to keep the tin content as low as possible The printers' alloys have played an important part in the history of our present-day publishing

Alloys used in linotype and similar machines are softer than those employed in cast type, running 2 5 to 3 per cent tin, 10 per cent antimony, 87 to 87 5 per cent lead Often slightly harder alloys are required These are obtained by increases in the antimony content and sometimes in the tin content These alloys have no prolonged period of solidification They pass almost instantly from the fluid to the solid state Purity of the constituent metals is very important Traces of copper cause the formation of hard copper-tin and copper-antimony constituents which solidify at higher temperatures and tend to clog up machines Zinc is also deleterious, inasmuch as it is not soluble in the alloy but forms spongy semi-solid masses which destroy the fluidity

of the metal Nickel, iron, sulfides, and oxides are always sources of trouble

In the monotype machines where single letters are cast in contradistinction to the linotype which casts a line of type at once, a good average alloy contains 8 per cent tin, 15 per cent antimony, and 77 per cent lead Tin reduces the melting point of the alloy and makes it flow more freely It toughens the final type, refining the structure and causing the formation of a compact, crystalline growth and a cast surface which is necessary for the production of type faces giving smooth and sharp definition

The constitution of alloys employed in the typograph, stereotyping, and plate casting is given in the table of alloys

SOLDERS

Tin-lead alloys in the shape of solders are widely employed in the sheet metal and plumbing trades and in the vast machine manufacturing industries Solders generally fall into one of three classes either tinman's or fine solder, in which tin and lead are in the proportion of 2 to 1, medium solder, where the proportion is 1 to 1, and plumber's solder, in which the proportion is 1 to 2 Commercial tinman's solder has a melting point of about 180°

A brief description of the characteristics and requirements of solders in general might be of interest at this point When cast into bars, solder should present a smooth and bright appearance free from oxide inclusions and bubbles Ductility should be as great as possible without sacrificing tensile strength, and vice versa Hardness and specific gravity are not of any great importance

The melting or solidification range is important This statement applies both to the extent of the range and to the actual temperature at which complete solidification occurs A rather narrow solidification range is desirable in soft solders in order that solidification may take place quickly The solder should have high fluidity at temperatures only slightly above its melting range For a "wiping" solder, on the other hand, a wide solidification range is necessary in order that the solder may remain in a pasty condition while the joint is being made, the solidification range should lie at temperatures low enough so that the wiping cloth will not burn during the operation Solders having a high melting point are valuable for use in soldering equipment that is to be used at elevated temperatures

Any alloy or metal that will readily alloy with other metals or alloys at ordinary soldering temperatures may be considered as a solder In

order to have commercial value for the purpose, it must be capable of readily forming joints of high tensile and shear strength together with high ductility The production of such joints depends not only on the strength and ductility of the solder itself, but is also largely dependent on the ease with which it alloys with or "wets" the metals to be joined The latter is especially important in machine soldering operations where soldering is carried on with extreme rapidity and capillary action is dependent upon very largely to draw the solder into the joint The property of "wetting" or flowing on the work is greatly affected by temperature and by the soldering fluxes used, and different solder alloys may require different temperatures and fluxes to give best results

In general, the thinner the layer of solder between the metals joined, the greater will be the strength of the joint, so long as the film of solder is continuous

The long period of solidification shown by plumber's solder is the reason for its usefulness The semi-plastic condition through which the alloy passes allows the production of the "wiped joint" so widely employed

Copper in small amounts ordinarily does not interfere with the working of solder, but when the percentage of copper is greater than 0 2, working difficulties are experienced It is often claimed that solders are improved by the addition of small amounts of antimony Specifications are often written to prohibit more than 1 per cent, although many tacitly permit up to 2 to 3 per cent

Solders are often judged commercially by the surface appearance of the cast solder bar An inspection of the mirror-like surface of a test ingot is the usual means of judging quality Surface spots are considered to be objectionable in fine solders, but are not so held in the case of plumber's solders

The percentage of the constituents in solders in commerce may vary widely The table of alloys lists a large number of solders of both low and high tin content

Recently considerable attention has been paid to the possible replacement of some or all of the tin in solders by cadmium [1] Although a number of articles appeared during the war advocating the use of cadmium in lead-tin solders, very little information of value can be found in the literature regarding the properties of solders containing cadmium In most of the published articles the cadmium seems to have been considered merely as a partial substitute for tin in a tin-lead alloy rather than as an essential constituent of a ternary alloy The primary

[1] *Proc Inst Metals Div , Am Inst Mining Met Eng ,* 1928, p 352

object of the substitution of cadmium for tin was to lessen the amount of tin required, at a time when the latter was scarce and high priced, and thus to produce a cheaper solder While this object was accomplished, the new properties resulting from a change from a binary lead-tin alloy to a ternary lead-tin-cadmium alloy were not given proper consideration in many cases

Tests by Swartz of the Research Department of the American Smelting and Refining Co showed that solders containing cadmium would make joints equal in strength to joints made with lead-tin solders, and that the cadmium alloys were suitable in other respects for use as solders Similar tests made with the same alloys to which 1 5 to 2 0 per cent zinc had been added showed that the addition of zinc in this proportion improved the properties of the alloys for this use In general, the investigation indicated the solders having compositions in the neighborhood of the ternary lead-tin-cadmium eutectic as being the best of the ternary alloys for most soldering work, though compositions varying rather widely from this may be more desirable for certain purposes

Fusible metals, practically all of which contain appreciable quantities of tin, have been used for boiler plugs, easily meltable inserts in sprinkler systems, and similar applications The fusible alloys can be manufactured with almost any desired melting point from 60° upwards The best known is Wood's alloy, containing 12 5 per cent tin, 12 5 per cent cadmium, 25 per cent lead, and 50 per cent bismuth Other typical fusible alloys are given in the table elsewhere in this chapter

PEWTER

Pewter is a subject on which little has been written It is generally considered to be an alloy of 80 per cent tin and 20 per cent lead French pewter used for drinking vessels is restricted to a maximum of 18 per cent lead

For centuries the work of the pewterer in England was controlled by the Worshipful Company of Pewterers This organization supervised individual workshops to the point of confiscating materials not up to the standard requirements Nevertheless, it appears that pewter specifications varied widely even under these conditions "Fine" pewter consisted of about 81 per cent tin and 19 per cent copper, with brass sometimes replacing the copper Common pewter was composed of about 82 per cent tin and 18 per cent antimony These alloys are white, relatively hard, and durable They will take reasonably good polishing and retain the finished surface under careful handling

Lead has always been a constituent of pewter, its proportion varying

up to 30 per cent, but commonly fixed at about 20 per cent Bismuth
and antimony are often added to reduce the melting point of the alloy
Very little antimony entered the pewters on the Continent Fi01avanti
used 88 per cent tin and 12 per cent lead for dishes Fiench compo-
sitions curtail the amount of lead to avoid the possibility of lead
poisoning due to the formation of lead acetate by the beverages, such
as acid wines, held in the vessels Zinc, in small amounts, has some-
times entered among the constituents of pewter

Recently specifications for the alloy in England have been supervised
and controlled by a government board, which maintains a high stand-
ard The lead content is restricted to approximately 10 per cent, a
qualification which is responsible for the return of a high-grade pewter
Britannia metal is a modern form of pewter, being principally a tin-
antimony alloy, containing no lead, but often copper and occasionally
small amounts of zinc Some representative compositions are given in
the table of alloys

The distinctive "ciy" of tin is considered by collectors to be of
value in judging the purity and quality of pewters It is supposed to be
altered by the presence of zinc and to a lesser extent by lead However,
a good solder containing more than 30 per cent lead will give quite a
pronounced tin cry

An example of the variation in purity is shown in the following
comparison A pewter plate used for printing music showed a perfect
engraving Analysis showed 27 3 per cent tin, 3 4 per cent antimony,
0 6 per cent copper, 68 7 per cent lead Contrasting sharply, examina-
tion of a very common looking tavern tankaid proved it to be 97 per
cent tin, the balance antimony with traces of copper and lead

In the manufacture of pewter, the widely varying melting points
of the constituent metals need to be taken into account Tin melts at
232° C , lead at 327° C , copper at 1083° C , and antimony at 630° C
It is clear that there is a great possibility of overheating the tin in the
melting Pewter is therefore made from tin-copper, tin-lead, and tin-
antimony alloys, whose melting points are lower than the mean of their
constituents The molten alloys are poured into the tin The result is
not a simple mixture or solution of the individual metals, but of several
constituent alloys which have different melting points and which solidify
in successive stages, the whole finally being cemented together by the
eutectic The reader is referred to the phase rule diagrams of the
tin-copper, tin-lead, tin-antimony, and the ternary system of these metals

The alloy is cast into ingots, then remelted and cast into molds
These may be dies of iron or bronze, or may be of a less durable nature,

as plaster and the like Permanent or "chill" molds are composed of
several sections These are so joined together that they may be sep-
arated to release the casting Care in the fitting of the sectors overcomes
to a great extent the tendency to form ridges on the casting at such
points Heating the mold prevents a sudden cooling of the alloy The
entrance of dross into the casting is to be carefully avoided The inner
surface of the die is lined with a finely powdered material, as oxide
of iron, mixed with a gum The pewter articles are next cold-worked,
a process which is usually finished, if not completely done, by hammer-
ing They may be polished to a bright finish Among the ancient crafts-
men, "touch marks" to identify the workman were stamped on the
completed article

Pewter is a comparatively durable alloy if properly handled It
tarnishes on exposure to air, but this tarnish or patina does not detract
from the value of the specimen Corrosion does not readily attack
pewter, nor is the alloy subject to "season cracking," a disintegration
brought about through hardening It may be cleaned with a compo-
sition of soap and kieselguhr, applied by means of a polishing bob The
ancient methods employed sand and often elm leaves or plants These
contained siliceous matter Unless cleaning materials are completely
removed from the joints of pewter objects, there is a tendency to loosen
these connections

DIE-CASTING ALLOYS

Tin is quite widely used in connection with zinc-base die-casting
alloys, in which the tin content may vary from 2 to 10 per cent Lead-
base alloys containing appreciable amounts of tin, up to as high as 20
per cent, are finding greater use, while the true tin-base alloys, because
of the high cost, are generally superseded by other metals having
cheaper constituents Of the tin-base metals which are employed, those
carrying high tin content are used more often than the low-tin-base
white metals Sometimes a tin-antimony alloy, containing 60 to 90 per
cent tin and the rest antimony, is die cast for valves

Toy metals from which small toys are die cast in large numbers are
often lead-base alloys containing an appreciable amount of tin

THERMAL EQUILIBRIUM DIAGRAMS

In the following pages the thermal equilibrium diagrams, at least
as far as the binary system are concerned, of tin and its alloys are given
Their study and the applications of the results of this work are finding
wider fields of usefulness throughout industry

Tin-Aluminum

Tin and aluminum alloy readily Small amounts of either metal have large effects on the properties of the other Tin increases the tensile strength of aluminum when alloyed with it and decreases piping in castings With too much tin, the alloys are brittle and easily oxidizable A 15 per cent tin alloy falls to powder after a few days Richards[2] described a strong malleable alloy with 10 per cent aluminum, which, after standing a few months, lost all its malleability It became as rotten as dried clay Annealing did not restore its strength If the alloy be fabricated into sheet, and portions of the sheet heated, small globules
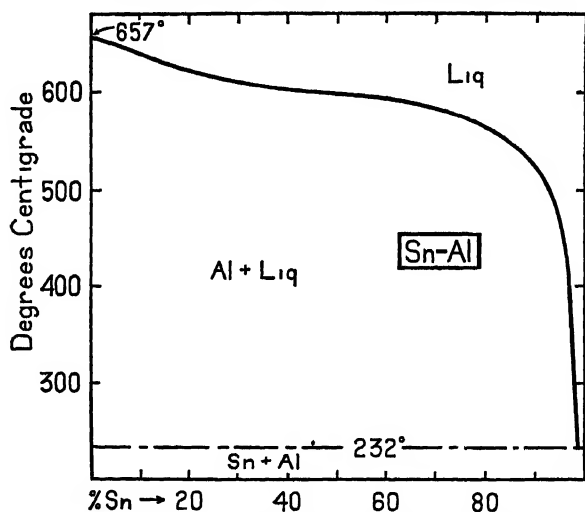
Fig 56 —Diagram of tin-aluminum system

sprout in all directions These have the same composition as the alloy E Heyn and E Wetzel[3] found that the length of a sample of tin with 0 5 per cent aluminum decreased for 28 days after quenching, and then increased, but at a slower rate, for the next 150 days

Tin added to aluminum gives sharp castings The high-tin alloys have been studied by Losana and Carozzi[4] Up to 5 per cent tin, the alloys can be cold rolled, but hot rolling is not successful above 200° C

Figure 56, due to Gwyer, gives the thermal diagram of the tin-aluminum system The curves seem to show simple solubility without compound formation Electrical conductivity studies do not show the existence of compounds

[2] "Aluminium," Philadelphia, 1896, p 525
[3] *Mitt Kaiser Wilhelm Inst Metallforsch ,* 1 19 (1922)
[4] *Gass chim ital ,* 53 546 (1923)

Alloys with 15 to 50 per cent aluminum are attacked by water at ordinary temperatures with the evolution of hydrogen

Tin in amounts below 2 per cent is used by some foundrymen in various casting alloys, such as those with copper, sometimes in an attempt to avoid cracked castings, sometimes to add ductility, or to give a white looking alloy Tin is a relatively high-priced metal Its use in aluminum alloys probably brings no advantage commensurate with the cost or which would not be readily obtained by other means On the other hand, small amounts of tin introduced unintentionally through the use of scrap would ordinarily not be considered a very detrimental impurity

Mortimer [5] states that in England a 7 per cent copper aluminum alloy may still contain up to 1 per cent tin The tin content was specified at one time, although it is not quite clear why it was ever included

The commercial use of tin-aluminum alloys is very small

In the ternary systems, the Cu-Sn-Al alloys have been investigated by Wahlert,[6] Stockdale,[7] Read, and Greaves [8] The Au-Sn-Al alloys were studied by Shepherd,[9] the Sn-Al-Zn system by Crepaz,[10] and Losana and Carozzi,[11] the Sn-Al-Cd, and the Sn-Al-Bi alloys by C R A Wright,[12] and the Sn-Al-Sb by W Campbell [13]

<div align="center">BINARY ALLOY DIAGRAMS</div>

TIN-ANTIMONY

The tin-antimony alloys are of great commercial importance, appearing in type metals, Britannia metal, and Babbitt for lining bearings Another element, such as lead, is generally added The tin in such materials is capable of infinite variation The antimony seems to be confined in commercial alloys to a maximum of about 25 per cent, inasmuch as larger quantities confer increased brittleness

Molten tin dissolves antimony, and the two elements unite without the evolution of light and heat The alloys can be made by fusing antimony sulfide with tin, although the usual manner is by mixing the molten metals

An alloy of 12 5 per cent antimony is stated to have a fine musical tone Up to 10 per cent antimony, the alloys are quite ductile, but at

[5] *Proc Am Soc Testing Materials,* (2) **22** 335 (1926)
[6] *Metall Erz ,* 18 298 (1921)
[7] *J Inst Met ,* 35 181 (1926)
[8] *J Inst Met ,* 15 264 (1916)
[9] *J Phys Chem ,* 8 114 (1904)
[10] *Giorn chim ind appl ,* 5 115, 285 (1923)
[11] *Gazz chim ital ,* (2) 53 546 (1923)
[12] *J Soc Chem Ind ,* 13.1017 (1894)
[13] *J Am Chem Soc ,* 26 1311 (1904)

25 per cent antimony the ductility is less than tin, at 50 per cent anti-mony the alloys are extremely brittle and can be readily powdered If small amounts of lead be present, the brittle alloys are more ductile

The tin-antimony alloys form the base of Britannia metal, which is mainly tin hardened with antimony in quantities of 6 0 to 9 2 per cent antimony Algiers metal has 10 to 25 per cent antimony An antimony content of 33 per cent ordinarily marks the extreme limit when the alloy is very hard Numerous modifications, alloyed with zinc, bismuth, lead, and copper, appear in commerce

The tin-antimony system was constitutionally examined two decades ago when the liquidus and solidus curves were fixed with fair accuracy
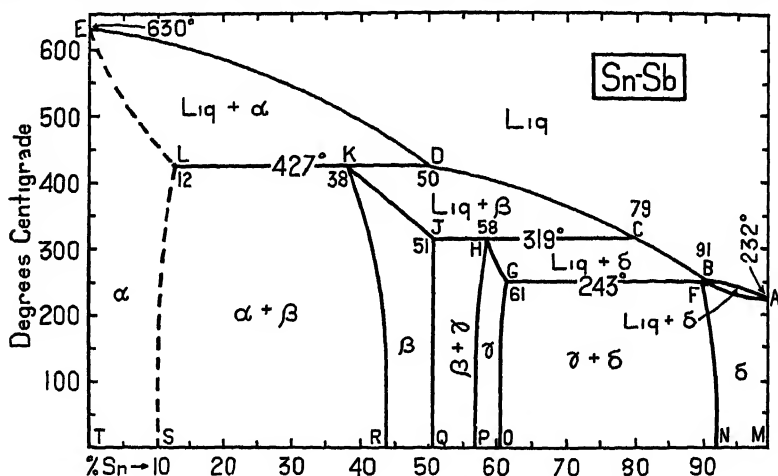
Fig 57 —Diagram of tin-antimony system

Little experimental attention has been given to the transformations in the solid state The system is given in Figure 57 Most of the solid solubility lines are from the hypotheses of Guertler

The liquidus curve, *EDCBA*, irregularly descends from the melting point of pure antimony at 630° C to the melting point of pure tin at 232° C Four solid solutions form the primary constituents which freeze out The alpha solid solution exists between the compositions of 0 and 50 per cent tin (100 and 50% antimony), the beta between 50 and 79 per cent tin (50 and 21% antimony), the gamma only over a small area, and the delta between 91 and 100 per cent tin (9 and 0% antimony)

The solidus curve *ELKJHGFA* is complex, due to three transfor-mation reactions at *K, H,* and *F* These are responsible for the tem-

perature horizontals at 427°, 319°, and 243° C The completely solid alloys consist of either a single solid solution or a mixture of two solid solutions The solid solubility curves in each case show that solubilities decrease with decrease in temperature

An explanation of one of the reactions will serve for all three shown in the diagram For example, alloys between the compositions of 12 and 38 per cent tin (88 and 62 per cent antimony) form a mixture of solid solutions beta plus alpha on freezing at 427° C There are three phases in equilibrium at the invariant point K The liquid metal, however, has an excess of tin over that indicated by K The liquidus there-
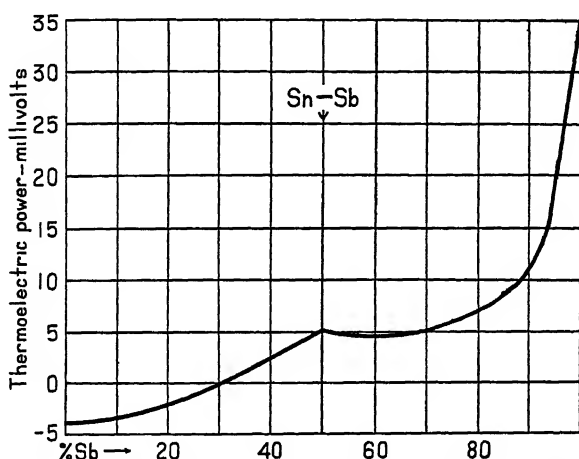
Fig 58 —Thermoelectric powers of the tin-antimony alloys

fore continues to slope from D to C The alpha solid solution, previously in equilibrium with the liquid metal, changes to the beta solid solution This is also in equilibrium with liquid metal in the composition range of 38 to 50 per cent tin (62 to 50 per cent antimony) and at 427° C

At 51 per cent tin, 49 per cent antimony, it is believed the SnSb compound exists It shows well formed cubic crystals Stead[14] states that alloys with 7 5 per cent antimony contain some of these crystals, and that they are particularly well formed in alloys with 25 to 40 per cent antimony Alloys of over 40 per cent antimony contain tabular crystals These crystals of SnSb may be considered responsible for the characteristic cubic structure observed in the gamma solid solution

[14] *J Soc Chem Ind*, 16 204, 506 (1897), 16 1111 (1898), *J Inst Metals*, 22 127 (1919)

Pushin [15] shows that there is an abrupt point on the e m f composition curve corresponding to SnSb

Gautier [16] and Matthiessen [17] showed that the specific gravity of the tin-antimony alloys is less than that calculated from the specific gravities of the components They therefore show expansion when alloyed

The thermoelectric powers of the tin-antimony alloys (tin metal and tin-antimony couples) were studied by Rollmann,[18] Naccari and Bellate,[19] as well as by Battelli [20] and Hutchins [21] The curve of the thermoelectric power is given in Figure 58 A definite break in the curve, corresponding to the compound SnSb on an atomic percentage basis, is found A similar break is shown in the curve of electrical conductivities (Fig 59), which had been investigated by Elsässer,[22] Konstantinoff and Smirnoff,[23] from whose results at 25° C the curve
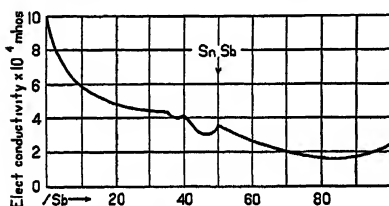
FIG 59 —Electrical conductivities of the tin-antimony alloys
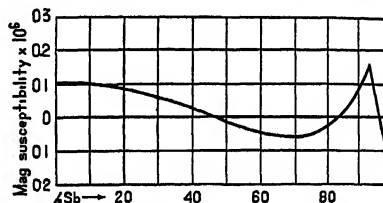
FIG 60 —Magnetic susceptibilities of the tin-antimony alloys

has been plotted The values for the magnetic susceptibilities of the tin-antimony alloys, as determined by Leroux,[24] have been used for the curve shown in Figure 60 It is interesting to note that the alloy of approximately 5 to 9 per cent tin and 91 to 95 per cent antimony shows greater magnetic susceptibility than all the other alloys, or pure antimony or tin

W Campbell [25] examined the tin-antimony ternary alloys with copper, silver, zinc, cadmium, aluminum, lead, arsenic, and bismuth For further detail the reader is referred to the literature

[15] *J Russ Phys Chem Soc*, 39 528 656 (1907)
[16] *Bull soc enc nat ind* (5), 1 1316 (1896)
[17] *Pogg Ann*, 103 412, 428 (1858), 110 21, 190 (1860), 130 50 (1867), *J Chem Soc*, 20 201 (1867), *B A Rep*, 1863 p 37
[18] *Pogg Ann*, 83 77 (1851), 84 275 (1851), 89 90 (1853)
[19] *Ellectricista*, 1 329, 362 (1877)
[20] *Mem accad torino* (2), 36 497 (1885), *Phil Trans*, 148 369, 383 (1858), 150 171, 161, 177 (1860), 156 861 (1866)
[21] *Am J Sci* (3), 48 226 (1894)
[22] *Wied Ann*, 8 455 (1879)
[23] *Internat Z Metallog*, 2 154 (1912), *J Russ Phys Chem Soc*, 43 1201 (1911)
[24] *Compt rend*, 156 1764 (1913)
[25] *J Am Chem Soc*, 26 1306 (1904)

TIN-ARSENIC

When powdered arsenic is stirred into molten tin, the union of the two elements is attended by the evolution of heat and light

Arsenic is appreciably soluble in tin but has little depressing effect on the tin melting point, tin, however, markedly affects the vapor pressure and melting point of arsenic In this system, pressure, usually considered as invariant in metal alloy systems, is a definite factor and variable The fusion equilibrium curves are quite complicated, a condition caused by arsenic vapor being one of the components at higher temperatures due to the high vapor pressure and subliming of arsenic
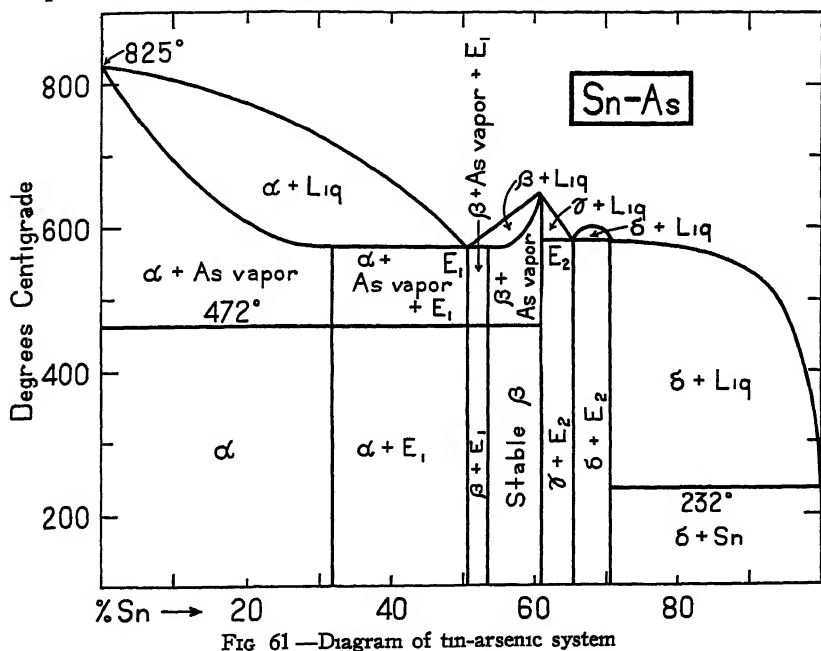
FIG 61 —Diagram of tin-arsenic system

The tin-arsenic alloys are quite brittle They are not of commercial interest of themselves, but become so in ternary systems The fusion equilibrium diagram is given in Figure 61

Mansuri [26] states that while the two metals alloy in all proportions, they form but two compounds, Sn_8As_2 and $SnAs$, as proved by two distinct maxima in the thermal equilibrium curve, by chemical analysis, and by photomicrographs The melting point of arsenic lies between 800° and 850°, but molten arsenic can be supercooled considerably

[26] *J Chem Soc*, 123 214 23 (1923)

At the concentration of 29 5 per cent arsenic (70 5 per cent tin), the alloy freezes at a single temperature and is the compound delta itself The rest of the system up to an alloy containing about 39 per cent arsenic (61 per cent tin) is of the usual eutectiferous type At that composition the compound SnAs is formed This compound forms a partly eutectiferous system with arsenic with the formation of the solid solutions beta and alpha, at both ends respectively It is these solid solutions that have arsenic vapor present as one of their constituents All alloys containing these solid solutions give a thermal arrest at 472° Alloys of tin with arsenic are very similar to those of tin with phosphorus in most of their properties and in their crystal structure The thermal curve of the tin-arsenic system is very similar to that of the tin-phosphorus system

The tin-arsenic alloys are quite hard, arsenic even in small amounts increasing the hardness of tin metal The alloys are white, sonorous if the arsenic be in not too great an excess They are usually brittle with appreciable arsenic content, as well as being decidedly crystalline, of a lamellar texture When fused in an open pot or kettle, arsenic is evolved and volatilized, the alloy concentrating in tin content When treated with hydrochloric acid, arsine (AsH_8) is evolved, but alloys with an excess of arsenic are not attacked by the acid

TIN-BARIUM

The alloys of tin and barium have been little studied They are difficult to prepare as a result of the rapid oxidation of the barium metal under ordinary atmospheric influences Even with protective layers of fluxes they are difficult to prepare With appreciable percentages of barium they are decomposed by water, leaving a tin skeleton They are of no industrial importance at the present time

The tin-barium system has not been thoroughly investigated It is stated that the alloys are similar to those of tin and calcium

TIN-BISMUTH

Binary alloys of tin and bismuth are seldom used industrially They are of considerable importance, however, in connection with fusible alloys, which contain either lead or cadmium or both in addition

The system has often been investigated, and still certain sections have not as yet been definitely established The thermal equilibrium diagram, as shown in Figure 62, is essentially of the simple eutectiferous type Two branches of the liquidus curve, *CB* and *AB*, meet at a eutectic containing 57 per cent tin, melting at 135° C

From 0 to 57 per cent tin, the primary constituent is the alpha solid solution of tin in bismuth From 57 to 100 per cent tin, the primary constituent is the beta solution of bismuth in tin

Bismuth-tin compounds are not formed

The solidus line passes through the points *CEBDA* Immediately after solidification, alloys between 0 and 1 4 per cent tin, 100 to 98 6 per cent bismuth, consist of the single alpha phase Those between 1 4 and 94 per cent tin, 98 6 and 6 per cent bismuth, consist of a mixture of alpha plus beta solid solutions Those running 94 to 100 per cent tin, 6 and 0 per cent bismuth, consist, immediately after solidification, of the single beta phase The exact form of the *CE* and *AD* sections of
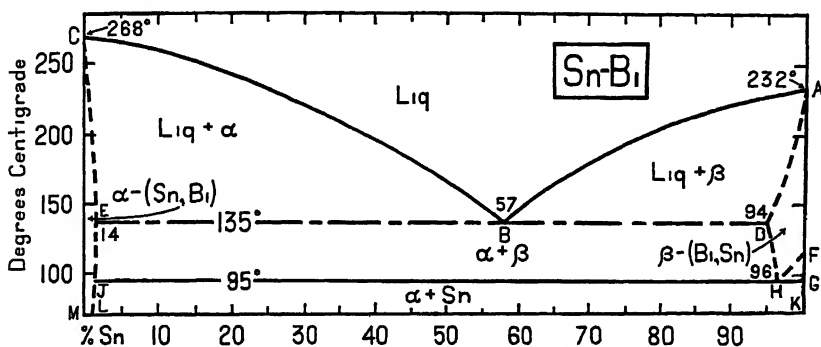
FIG 62 —Diagram of tin-bismuth system

the solidus curve has not as yet been completely and definitely determined

Tin is less able to keep bismuth in solution below the eutectic temperature Eutectoid inversion takes place at 95° C The dotted lines *FH* and *DH* give the approximate limits of solid solubility This transformation can be detected by sensitive cooling curve methods (in alloys covering a wide range), as shown by the transformation horizontal *JHG* Below 95° C, alloys from 2 to 100 per cent tin are duplex in structure They contain pure tin and alpha (tin in bismuth) solid solution

The line *EJL* approximately indicates the solubility limit of the alpha solution This section of the diagram has been very little investigated

The results of Schultze [27] for the thermal and electrical conductivities of the tin-bismuth alloys are plotted in Figure 63 The addition of bismuth to tin markedly lowers both the thermal and electrical con-

[27] *Ann Physik*, (4), 9 555 (1902), "Ueber das Verhalten einiger Legierungen zum Gesetz von Wiedemann und Franz," Dissertation, Marburg, 1902

ductivities of the metal There aie no maximum points in the curve
The addition of small amounts of tin to bismuth loweis its thermal
and electrical conductivities, but increasing amounts of tin cause bet-
ter thermal and electrical conductivity Caswell[28] states that there is
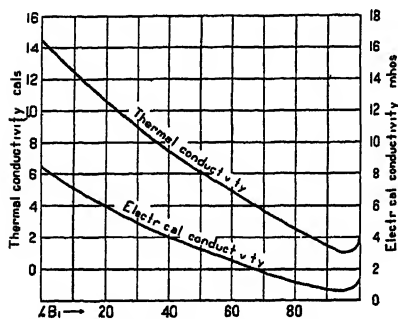
FIG 63 —Thermal and electrical con-   FIG 64 —Thermoelectric values for tin-
  ductivities of the tin-bismuth alloys   bismuth alloys
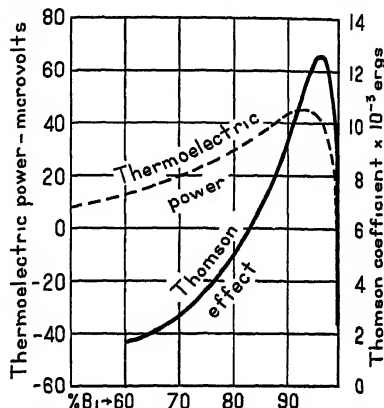
a remarkable increase in the Thomson effect when very small amounts
of tin are added to bismuth, e g , the value is 58 millivolts per degree
C for pure bismuth, and 676 millivolts for 1 per cent tin alloy Beyond
about 2 per cent, the value of the Thomson effect decreases

A large number of workers, among them being Ettinghausen and
Nernst,[29] studied the thermoelectric propeities of tin-bismuth alloys
The results are plotted in Figure 64 Alloys of approximately 9 per
cent tin content show the highest e m f values, while those of about
5 per cent tin show the gieatest Thomson effect No compounds seem
to be indicated in either the conductivity or thermoelectric curves of the
tin-bismuth alloys The results of Gnesotto and Binghinotto[30] for the
magnetic susceptibilities of the alloys aie of scientific interest only The
curve, given in Figure 65, is without sharp maxima or minima

TIN-CADMIUM

Cadmium may be alloyed in small quantities with tin as a means of
improving the pure metal for certain uses The binary system at the
present moment, however, is of little more than theoretical interest

Bucher[31] stated that tin and cadmium are mutually soluble in each
other in the solid state to the extent of about 3 per cent

28 *Phys Rev* 12 231 (1918)
29 *Wied Ann ,* 33 474 (1888)
30 *Atti ıst Veneto* (8) 12 1382 (1910)
31 *Z anorg Chem ,* 98 106 (1916)

The thermal diagram is given in Figure 66. It is of the same type as that of the tin-bismuth alloys. Tin and cadmium form a eutectic at 72 per cent tin, 28 per cent cadmium, with a melting point of 177° C. The primary constituent between 0 and 28 per cent cadmium is the gamma solid solution of cadmium in tin; and from 28 to 100 per cent
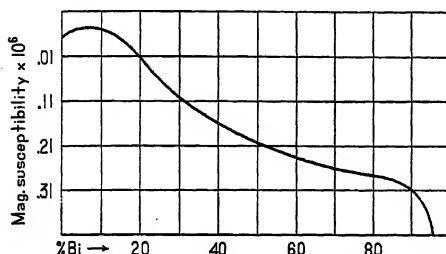
Fig. 65.—Magnetic susceptibilities of the tin-bismuth alloys.

cadmium, the first phase to crystallize is the delta solid solution of tin in cadmium. No definite compounds are formed between the two metals.

The solidus line is *ADBEC*. All alloys between 9 and 97 per cent cadmium (91 to 3% tin) complete their solidification at 177° C., the eutectic temperature.
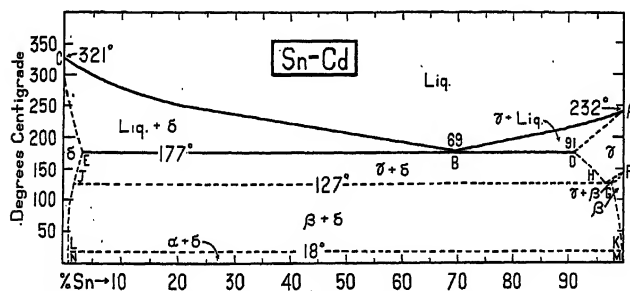
Fig. 66.—Diagram of tin-cadmium system.

The solid solution gamma (cadmium in tin) shows a rapidly decreasing power of holding cadmium in solution as the temperature decreases. There is a eutectoid inversion at 127° C. which produces beta solid solution of cadmium in tin. The line *GHJ* is the limit of the structural transformation. This has been observed over a wide range. Alloys between 9 and 97 per cent cadmium consist of the gamma plus delta solid solutions in the temperature range of 177° to 127° C.

The beta solid solution shows a gradually diminishing power of holding cadmium in solid solution, becoming practically zero at 18° C The line *GKM* shows the reduced solubility of the cadmium in the tin On the other side of the diagram, correspondingly the line *EJLN* shows the lessening of the solubility of tin in cadmium with fall in temperature

The allotropy of tin which is responsible for the polymorphic modification of gamma to beta solid solutions is again responsible for another transformation at 18° C to the alpha form, which corresponds to the change of white to gray tin

It is interesting to note that an alloy of two parts tin, one part cadmium, cut into chips on a milling machine, about 0 05 mm thick, 12 mm long, 1 to 3 mm wide, and closely packed, without jamming, into a tube 1 cm in diameter, 50 cm long, was found by Welo [32] to be an effective bar to the passage of mercury vapor from a mercury high-vacuum pump to the vessel to be exhausted This was shown by means of spectrograms taken after allowing the pump to stand connected to the exhausted vessel through the tube containing the alloy

The ternary system Sn-Cd-Sb was studied by W Campbell,[33] the Sn-Cd-Zn by Rader,[34] the Sn-Cd-Bi by Spring,[35] and Andrews and Johnson,[36] and Stoffel,[37] who found the eutectic at 103 7° C of 33 2 per cent tin, 27 5 per cent cadmium, and 39 3 per cent lead

Tin-Calcium

There has been considerable study of the tin-calcium alloys Moissan [38] stated that when tin is heated to temperatures above its boiling point, it unites with calcium to form a crystalline alloy Donsky [39] found that tin dissolved calcium at 650° C

The thermal equilibrium diagram of the system is given in Figure 67 The addition of calcium to tin produces a sharp rise in the freezing point The liquidus curve rises from the melting point of pure tin (232° C) to a maximum of 627° C, corresponding to the compound Sn_3Ca, corresponding to 10 1 per cent by weight of calcium From here the liquidus falls slightly to a eutectic point (between Sn_3Ca and $SnCa$) at 609° C This corresponds to 31 2 atomic per cent calcium The horizontal line at 609° C is part of the solidus line of the system From the eutectic, the liquidus curve rises to 987° C, the melting point of the SnCa compound

[32] *Phys Rev* (2) 10 583 (1917)
[33] *J Am Chem Soc* 26 1313 (1904)
[34] German Pat 72,683 (1891)
[35] *Ber* 15 595 (1882)
[36] *J Inst Metals*, 32 385 (1924)
[37] *Z anorg Chem*, 53 137 (1907)
[38] *Compt rend*, 127 584 (1898)
[39] *Z anorg Chem*, 57 185 (1908)

This corresponds to a slight break in the curve, which, however, is not the maximum. The liquidus continues to rise to a maximum at 1122° C., corresponding to the compound $SnCa_2$. The remainder of the diagram is of the eutectic type, the constituents being $SnCa_2$ and pure calcium. From the maximum, the curve drops to a eutectic at 759° C., of 81.41
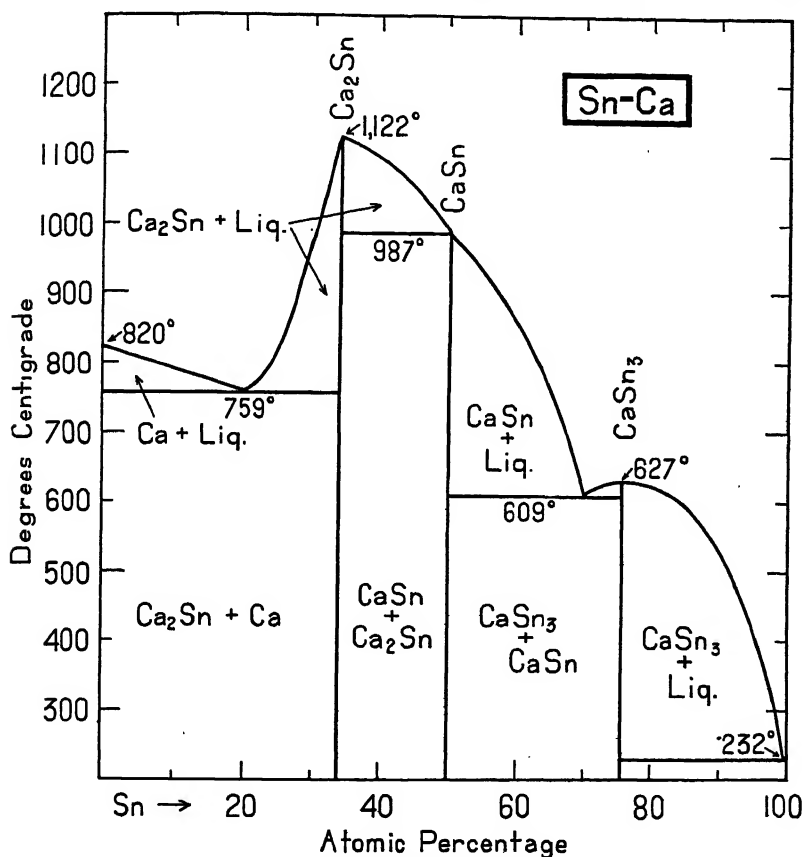
Fig. 67—Diagram of the tin-calcium system.

atomic per cent calcium. The liquidus then rises to 820° C., the melting point of pure calcium.

No evidence of solid solution has been found in the study of the system. As a result, the solidus is simple. All of the tin-calcium compounds are readily acted upon by water and atmospheric influences. The alloys are all white. The crystals of the tin-calcium compound cleave into thin plates a little paler in color than mercury. The alloys containing

up to 4 per cent calcium are harder than tin and fairly tough With further increase of calcium they become brittle Tin-calcium alloys have been proposed for use as aluminum solders

The tin-calcium alloys in general are rapidly attacked by water, air, and dilute acids The alloys at present have practically no industrial applications as binary alloys, but are of considerable theoretical interest

TIN-CARBON

Moissan [40] stated that tin does not unite directly with carbon to form carbides Practically no work has been done at low temperatures on the solubility of carbon in tin It does not appear that carbon-tin compounds do form at low temperatures, or that carbon has any measurable solubility in the metal
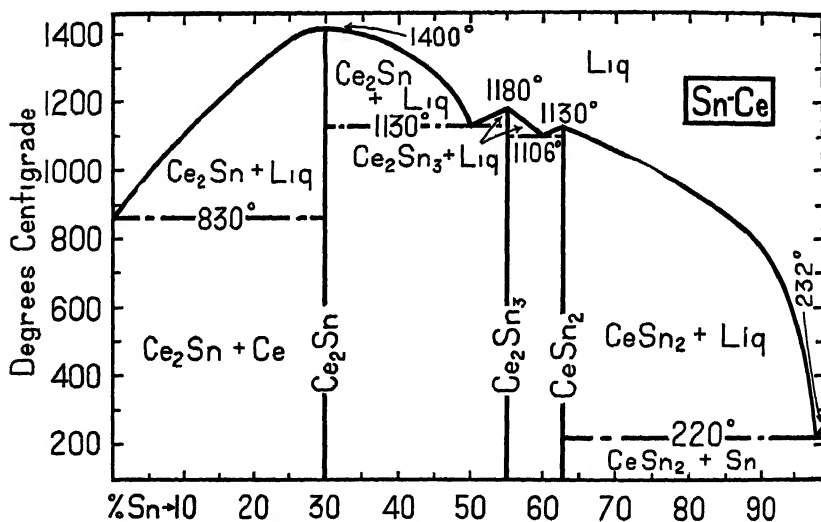
FIG 68 — Diagram of tin-cerium system

TIN-CERIUM

The thermal diagram of the tin-cerium alloys is shown in Figure 68 The freezing point of cerium is raised by the addition of tin to reach a maximum, at 30 per cent tin, of 1400° C This point corresponds to the compound Ce_2Sn Additions of tin lower the melting point of the compound until a eutectic is reached at 1130° C, between Ce_2Sn and Ce_2Sn_3 The latter compound occurs at a second maximum in the curve at 56 per cent tin, at a melting point of 1165° C A third compound, $CeSn_2$, is formed at 64 per cent tin, melting at 1135° C

[40] *Bull soc chim* (3), 13 959 (1859), *Compt rend*, 125 841 (1897)

Small amounts of cerium depress the freezing point of tin The alloys of tin and cerium tarnish rapidly, even when polished and covered with oil They are very unstable against corroding influences All the alloys containing less than 80 per cent tin are pyrophoric The alloys above 50 per cent cerium produce showers of sparks when merely scratched with a hard object The Ce_2Sn compound has the maximum hardness, about 6 on the Von Moh scale It is very unstable in air, and vigorously reacts with water

TIN-CHROMIUM

These alloys are as yet only of theoretical importance Neither chemical compounds nor solid solutions are stated to be formed, according to the data of Pushin [41] In the lower chromium ranges, the alloys are very soft and resemble tin Only those rich in chromium are hard

TIN-COPPER

The tin-copper alloys are of such great practical importance in the non-ferrous industries and are of such a complex nature that it occasions no surprise to find an extensive record of careful investigation in this field The early work of Heycock and Neville [42] on these alloys has been accepted as one of the classical researches in metallography It is remarkable how closely their results agree with work performed with apparatus equipped with every modern refinement

The presence of tin hardens copper The resulting alloy can take a high polish Its melting point is comparatively low, and when melted it can be cast very well The addition of a small amount of tin to copper, however, prevents the product from being easily fabricated by hot rolling If more tin be used, the alloy is not malleable when cold The term "bronze" is applied to the alloys of copper and tin Bronze is tempered by heating it to the required temperature and rapidly cooling in water This is the reverse of the process employed in tempering steel Modern bronzes are rarely simple binary alloys They are usually ternary or quaternary, and sometimes even more constituents are added Among the commercial varieties of bronze are the so-called gun metals which were formerly much employed in the construction of ordnance and artillery weapons The preferred mixtures vary widely among the different countries, usually from 8 to 11 parts of copper to one of tin The typical alloy is 90 copper, 10 tin The thermal history of the alloy is almost as important as the knowledge of its chemical composition

[41] *J Russ Phys Chem Soc*, **39** 353 99 (1908)
[42] *Phil Trans*, **189** (A) 63 (1897), **202** (A) 1 (1903), *Proc Roy Soc (London)*, **71** 409 (1903)

Gehlen [43] stated that if the two elements of tin and copper be simply fused together, bronze is produced If the mixtuie be not stirred, two liquid layers containing very different proportions of the two metals are formed The combination is effected without the production of heat or light Spring [44] stated that the alloy can be formed by subjecting a mixture of powdered tin and copper to high pressure
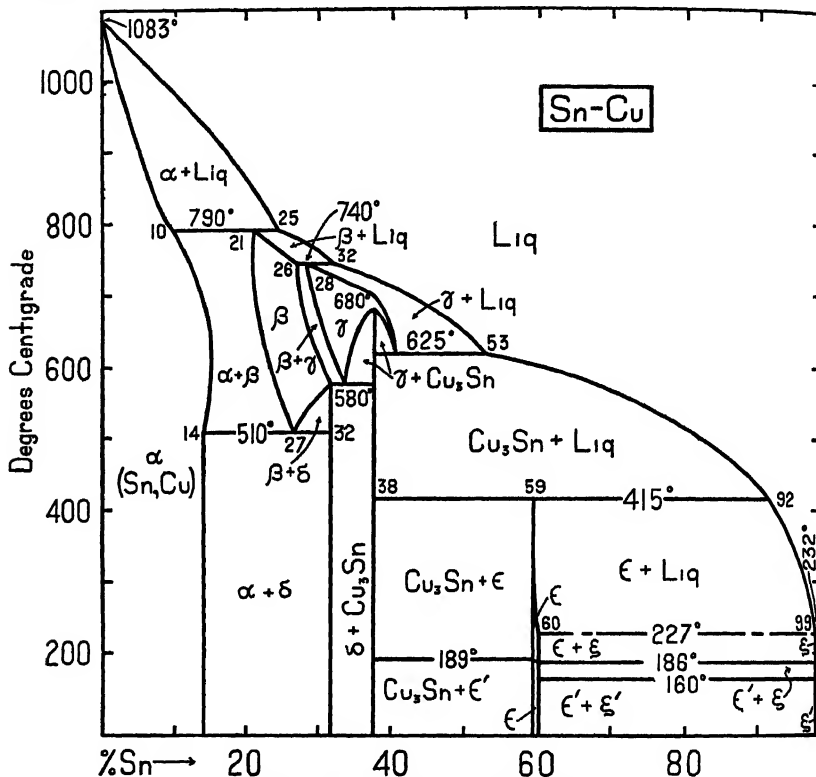
FIG 69 —Diagram of tin-copper system

The thermal equilibrium diagram for the bronzes is one of the most complicated binary systems known Figure 69 gives the data, the foundation of which at least was laid by Heycock and Neville,[45] who studied the freezing point curves of the alloys in 1903 More recently the alloys containing 0 to 50 per cent copper have been studied by J L Haughton,[46] who not only reviewed all previous investigations but in his own work

[43] *Schweigger's J* , **20** 353 (1817)
[44] *Z phys Chem* , **15** 65 (1894), *Bull Acad Belg* (3), **28** 23 (1894), (3) **37** 790 (1899)
[45] *Phil Trans* , **202** 1 (1903)
[46] *J. Inst Metals*, **13** (1) 222 (1915), **25** (1) 309 (1921)

made use of long-period annealings, which are necessary to insure true equilibrium conditions

Referring to the thermal equilibrium diagram, the melting point of copper is markedly affected by the addition of small amounts of tin The area represented by alpha is a solid solution of tin in copper The concentration of the tin in the copper varies with the temperature, being about 10 per cent at 790° and increasing gradually to 14 per cent at 510° The liquidus curve slopes from the melting point of copper at 1083° to a point represented by the junction of the temperature line of 790° and the tin percentage line of 25, where there is a break in the curve The area under this curve consists of the alpha constituent of tin in copper plus liquid In this area, the alpha crystals are stable in contact with the molten alloy Directly underneath this area represented by alpha plus beta are found mixed crystals of alpha and beta bronze, and directly alongside is an area in which we find solid beta bronze Under the liquidus curve, running from the junction point of 790° and 25 per cent tin to 740° and 32 per cent tin, is a small area were the beta bronze crystals are in stable equilibrium with the molten alloy The liquidus curve then drops from the junction point of 740° and 32 per cent tin to 625° and 53 per cent tin Under this curve we find an area in which gamma bronze is in stable equilibrium with the liquid alloy Directly adjoining is a small area in which solid gamma bronze is stable Between the beta and the gamma bronze areas there is a thin corridor in which we find mixed crystals of beta and gamma bronze Adjacent and below this there is another small area existing between 510° and 580° and 27 and 32 per cent tin, where mixed crystals of solid beta and delta bronze are found Directly adjoining the area of mixed crystals of beta and gamma bronze we find an irregular region in which gamma bronze and crystals of the compound Cu_8Sn are in stable solid equilibrium In a rectangular region bounded by the temperature line of 580° at one end and 0° at the other, 32 per cent tin on one side and 38 per cent tin on the other, we find a mixed crystal area of delta bronze and the compound Cu_8Sn Adjoining this on the left, between the temperature lines 510° at one end and 0° at the other and bounded on the left by the line represented by 14 per cent tin and on the right by 32 per cent tin, we find a rectangular region in which mixed crystals of alpha and delta bronze are stable The liquidus curve drops from the junction point of the temperature line 625° and 53 per cent tin to a point represented by the temperature line of 450° and 92 per cent tin, and then to a eutectic point at 227° and 99 per cent tin, from whence the curve rises to the melting point of pure tin at 232°.

An exceedingly careful piece of work by Gurevich and Hromatko [47] in which a delicate cooling curve method was used, placed the eutectic at 1 per cent copper and 227 1° C At 625° the primary constituent, gamma bronze, reacts with the liquid to form the compound Cu_8Sn This is in stable equilibrium with the molten alloy in the area under the liquidus curve from 38 to 92 per cent tin, and between the temperature ranges of 625° and 415° The compound Cu_3Sn reacts with the liquid along the solidus curve between 92 and 99 per cent tin and below 415° to form the constituent epsilon bronze, which is in equilibrium with the liquid between 59 and 99 per cent tin and between the temperatures of 415° and 227° At 415°, between 38 and 59 per cent tin and in an area represented at the bottom by 189°, the compound Cu_8Sn plus the liquid reacts to give mixed crystals of Cu_8Sn and epsilon bronze Below 189° there is an area in which the compound Cu_8Sn plus epsilon prime bronze is formed The epsilon bronze constituent exists alone only in a very small area of thin vertical cross section, as represented at approximately 59 to 60 per cent tin

Although earlier workers assumed that copper was totally insoluble in solid tin, Haughton found that the constituent represented by the solution of copper in tin did not appear in alloys annealed for 68 hours at 195° C until the copper content exceeded 0 23 per cent

Between 60 and 100 per cent tin and below 227° there are a number of transformations in the solid state At 227° the epsilon bronze reacts with the liquid to form mixed crystals of epsilon and xi solid solutions At 186° there is a hypothetical transformation of the epsilon to epsilon prime crystals This is based largely on the determinations of thermal resistance, but microscopic examination shows no difference between the two solid solution structures X-ray analysis should be helpful in further elucidating this question At 160° there is another transformation of the xi bronze to xi prime

The solidus curve of the bronzes is quite complicated and can be only approximately indicated In the ranges of low tin content, it drops from 1083° to a point represented by 790° and 10 per cent tin, proceeding horizontally at this temperature level to 21 per cent tin, and from there dropping to 740° and 26 per cent tin, again traveling horizontally to 28 per cent and dropping in an irregular manner to the temperature level of 625° and about 42 per cent tin It may then be imagined to travel horizontally along the temperature level of 625° to 38 per cent tin, dropping to the temperature level of 415° where it travels at this point horizontally across to 59 per cent tin, dropping again to 60 per cent tin

[47] *Trans Am Inst Mining Met Eng*, 64 227 (1920)

and the temperature level of 227°, horizontally across to 99 per cent tin, from whence it rises to 100 per cent tin at 232° In the light of the diagram and the numerous changes which occur with different thermal conditions, the great importance of the thermal history of a bronze as affecting its physical characteristics can be readily understood

Only one compound, Cu_8Sn, is shown on the equilibrium diagram It appears as bluish-grey or bluish-white lamellæ It is rapidly attacked by hot concentrated hydrochloric acid According to Mallet [48] the color of the copper-tin alloys containing 82 81 to 84 29 per cent of copper is reddish yellow, with 78 97 to 81 10 per cent, yellowish red, with 72 80 to 76 29 per cent, pale red, with 68 21 per cent, ash grey, 61 69 per cent, dark grey, with 51 75 per cent, greyish white, 34 92 per cent, white, becoming still whiter with increasing proportions of tin According to E Heyn and O Bauer,[49] the fracture of alloys which have been cooled rapidly has a uniform color, but if slowly cooled, there may be grey and yellow flecks R Mallet and J Rieffel [50] found that the fracture of alloys with 84 29 to 81 10 per cent copper is fine grained, with 78 97 per cent, vitreous and conchoidal, with 76 29 per cent, vitreous, with 72 80 to 68 21 per cent, conchoidal, with 61 69 per cent, lamellar and granular, with 51 75 per cent, vitreous and conchoidal, with 34 92 per cent, lamellar and granular, with 21 15 to 15 17 per cent, vitreous and granular, with 11 82 per cent, vitreous and lamellar, and with 9 68 per cent, earthy H Behrens [51] said that the alloy with 15 to 25 per cent of tin is fine grained, with 25 to 40 per cent tin, conchoidal

The alloys used in the manufacture of bells in the so-called bell metals contain copper from 74 to 85 per cent and tin from 15 to 26 per cent Other proportions are used to produce different sounds, and other metals, such as zinc, iron, lead, bismuth, silver, antimony, or manganese, may be added either for cheapness or to produce a special tone The typical alloy is 80 20 The sound from brass bells is of inferior quality In some of the white table bells tin is the dominating component Some white alloys   ally approximating Cu_4Sn, admit of a brilliant polish These were formerly used for mirrors and hence were called speculum metals They are sometimes used in the construction of mirrors for optical instruments Their composition ranges from 30 to 34 per cent tin and 62 to 69 per cent copper In some cases lead, zinc, arsenic, silver, nickel, or antimony has been added The typical alloy is 70 30 The term art bronzes, is applied to alloys which are employed for statuary, vases,

[48] *Proc Roy Irish Acad ,* 2 95 (1842), *Phil Mag* (3), 21 66 (1842)
[49] *Mitt Materialprufungsamt,* 22 137 (1904), *Z anorg Chem ,* 45 68 (1905)
[50] *Compt rend ,* 37 450 (1853)
[51] "Das mikroskopische Gefuge der Metalle und Legierungen," Hamburg, 1894, *Versl Akad Amsterdam* 2 79 (1894)

and ornaments of all kinds In a number of statues the proportion of
copper ranges from 72 to 91 per cent, tin 0 15 to 10 2 per cent, zinc 0 1
to 26 per cent, lead up to 3 per cent, and small proportions of iron, nickel,
and antimony

TIN-GOLD

Small quantities of tin have considerable effect on the ductility of
gold They do not, however, make it brittle Tin quite markedly affects
the color of gold In the proportion of 11 parts of gold to 1 of tin, an
alloy of a pale yellow color, only slightly malleable and with a fine-
grained structure, is produced Its specific gravity is 17 307, indicating
that the volume is less than the sum of the volumes of the constituents
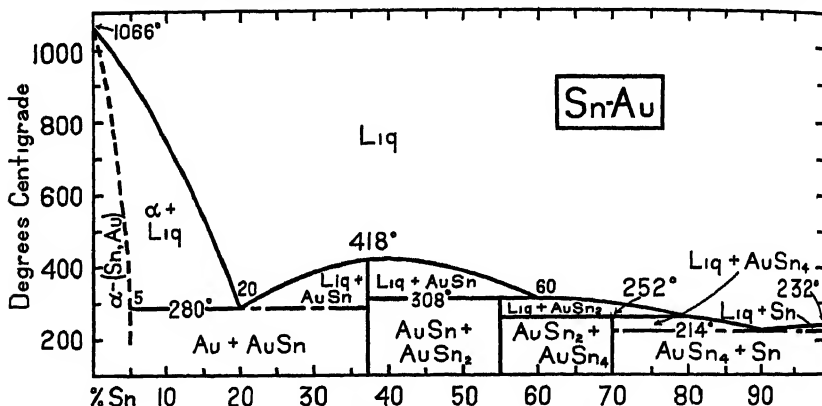
FIG 70—Diagram of tin-gold system

The thermal equilibrium diagram for the tin-gold alloys is given in
Figure 70 The addition of tin to gold lowers the melting point rapidly,
causing it to fall from 1066°, the melting point of gold, to a eutectic point
at 280° where the tin concentration is 20 per cent This eutectic has for
its constituents gold on one side and the compound AuSn on the other
From the eutectic, the freezing point curve rises to a well-defined maxi-
mum at 418°, corresponding to 37 63 per cent of tin and representing
the compound AuSn This is a silver-grey material more brittle than
gold and harder than either gold or tin Its electrical conductivity is
greater than that of all the tin-gold alloys excepting those containing
more than 95 per cent gold The compound AuSn is as resistant as gold
ordinarily is to the action of sulfuric, nitric, or hydrochloric acid, and is
only slowly attacked by aqua regia The liquidus curve, after passing
through the maximum at 418°, falls to a second eutectic at 214°, corre-

sponding to 90 per cent tin, then rises to 232°, the melting point of tin Between the maximum at 418° and the eutectic at 214°, there is a break in the curve at 308° and 60 per cent tin, corresponding to the compound $AuSn_2$ This appears as large crystals in the slowly cooled alloy It is as resistant to corrosion by the mineral acids as is the AuSn There is a second break at 252° and 80 per cent tin, corresponding to the compound $AuSn_4$ This compound is attacked by nitric acid and is colored brown as a result The same does not hold true for the $AuSn_2$ compound The solidus curve drops from 1066° and 100 per cent gold along a hypothetical line to a point represented by the junction of the 280° temperature level and 5 per cent tin, the area under the curve representing a solid solution alpha of tin in gold In the area between the solidus and the liquidus curves, the constituent alpha is in equilibrium with the molten metal The alloys containing 5 to 37 63 per cent tin all freeze at the eutectic temperature 280° and show the crystalline structure of gold mixed with the AuSn compound The solidus curve continues along the temperature level of 280° to 37 63 per cent tin, then rises to 308°, continuing at this temperature level to approximately 55 per cent tin In the area between the solidus from 20 to 37 63 per cent tin and the liquidus curves, we find the compound AuSn in equilibrium with the molten alloy The same holds true from 37 63 to 60 per cent From 37 63 to 55 per cent at 308°, the liquid and the compound AuSn react so that the solid phase consists of a mixture of the compounds AuSn and $AuSn_2$ From 55 per cent tin to 70 per cent tin, the solidus continues at the temperature level of 252° The area between the liquidus and the solidus shows the compound $AuSn_2$ in equilibrium with the molten alloy, and in the solid phases between 55 and 70 per cent tin the alloy consists of a mixture of the compounds $AuSn_2$ and $AuSn_4$ From 70 to 100 per cent tin, the solidus continues along at the temperature level of 214°, the area between the solidus and liquidus curves consisting of the compound $AuSn_4$ in equilibrium with the molten alloy, and the solid phases below 214° consisting of the compound $AuSn_4$ plus tin crystals From 90 to 100 per cent tin, the area between the solidus and the liquidus consists of tin in equilibrium with the molten alloy, and in its solid phases below 214° consists of mixtures of tin and the $AuSn_4$ compound

The tin-gold alloys have at times found use as cheaper substitutes for the more expensive noble metal applications for resistance to corrosion and chemical attack Infrequently gold-tin alloys have been used in jewelry and for decorative work Their commercial use is very limited Tin is often plated on "white gold" to overcome unevenness in color

Tin-Indium

Indium dissolves rapidly in molten tin Heycock and Neville [52] meas-
ured the freezing points of the alloys containing small amounts of indium
They are only of theoretical interest and have no commercial applications

Tin-Iron

The tin-iron alloys are not important industrially as a result of their
use as alloys, but their study is of decided interest inasmuch as their
formation at high concentrations of iron and tin is a source of con-
siderable difficulty in tin metallurgy and the winning of tin from fer-
ruginous ores They cause particular difficulty in the smelting of the
complex vein ores such as the Bolivian Their formation at low concen-
trations of iron in tin is of considerable importance in the manufacture
of tin plate

The early work on the system was done by Isaac and Tammann [53]
The complete system is given in Figure 71 The work of Wever and
Reinecken [54] explains to a considerable extent the reactions occurring
in the manufacture of tin plate In the discussion of this portion of
the work, we will refer largely to the right-hand side of the diagram
in connection with the alloys of 0 to approximately 20 per cent iron
Wever and Reinecken concluded that tin and iron are completely
miscible in the liquid state Former investigators had stated that the
miscibility was only partial Solidification of the tin-rich alloys begins
in the area shown in the diagram as Fe_3Sn plus liquid, along the solidus
line at 890° by the crystallization of an iron-tin compound out of the
melt At 890°, between 81 and 96 per cent tin, a peritectic reaction gives
rise to the compound $FeSn_2$ containing 81 per cent tin For alloys with
a tin content greater than 81 per cent, complete solidification does not
occur until a temperature slightly below the melting point of tin is
reached This temperature is as yet undetermined Wever and Reinecken
found thermal changes, which they attributed to polymorphic transfor-
mations in the compound $FeSn_2$, at 780°, 755°, and 490° At ordinary
temperatures the tin-iron alloys between 81 and 100 per cent tin consist
of a matrix of a solid solution of a very small amount of iron in tin
Crystals of the compound FeSn are embedded in this matrix At the
present date no reliable data are available as to the solubility limit of
iron in tin It is believed that at the best it is only a few hundredths

[5] *Chem News*, 59 175 (1889), *J Chem Soc ,* 55 666 (1889)
[53] *Z anorg Chem ,* 53 281 (1907), Guertler "Metallographie," Berlin, Verlag Gebr Born
traeger, 1911, Bd 1, Tl 1, p 642
[54] *Mitt Kaiser Wilhelm Inst Eisenforsch ,* 7 69 (1925), *Stahl Eisen,* 46 51 (1926), *Z
anorg allgem Chem* 151 349 (1926)

of a per cent Hot-dipped tin coatings show an alloy layer immediately adjacent to the iron base, with an outer layer of tin covering this alloy Inasmuch as only relatively low temperatures are used in tinning, and
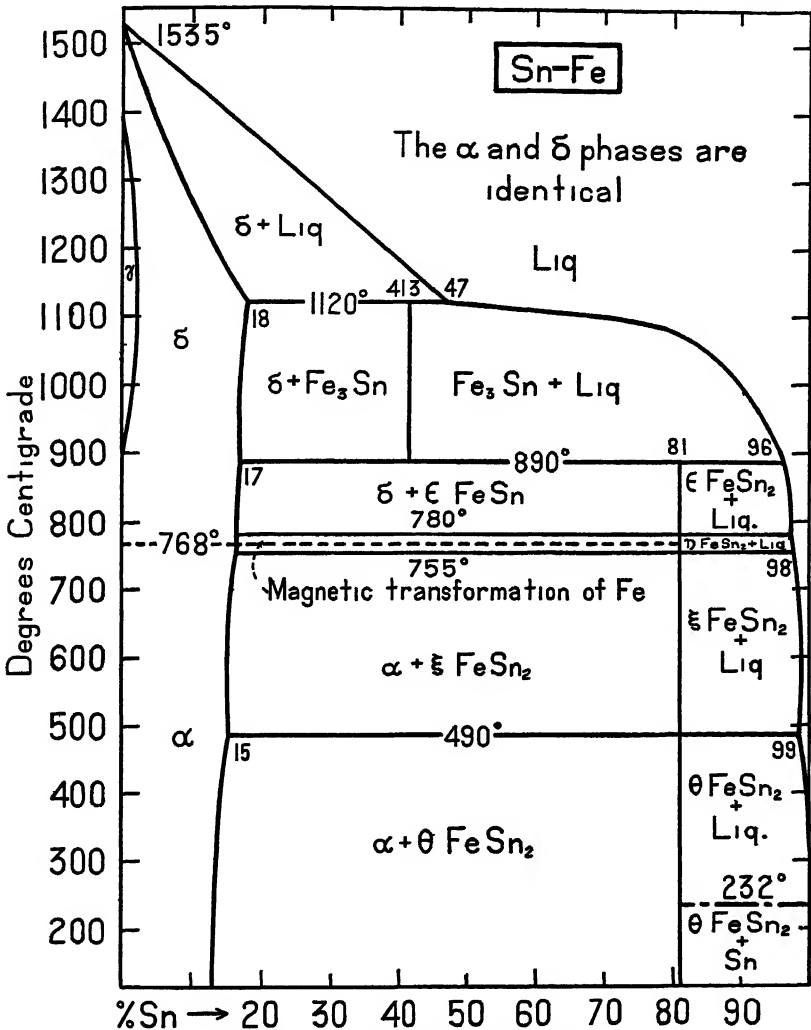
FIG 71—Diagram of tin-iron system

the operation is one of a short time period, the alloy layer in tin plate is exceedingly thin Often no evidence of it can be detected in metallographic sections of the coated sheet Very careful polishing and etching of the slightly bent surface of a sheet will usually demonstrate its

presence The alloy layer appears as a bluish film underlining the layer of tin which comprises the body of the coating

A method for determining the amount of alloyed tin in tin coatings has been devised by Kohman [55] The unalloyed tin readily dissolves in a hot solution of sodium plumbite, while the iron-tin alloy does not dissolve nearly as readily The percentage of alloy in a tin coating on ordinary coke plates is readily increased by keeping the steel sheet immersed in molten tin and allowing it to come to the temperature of the tin bath prior to passage through the tinning machine Kohman found that in ordinary commercial charcoal plate the alloyed tin constituted about 5 per cent of the weight of the coating, while in commercial coke plate the amount of alloyed tin was about 17 5 per cent

Rawdon [56] states that the effect of the alloyed tin upon the service behavior of the coated iron with respect to corrosion is of no practical importance, inasmuch as the compounds of tin and iron bear the same general electrochemical relation toward iron that tin does He further states that the alloy formation does not increase the corrosion resistance, since the alloys, like tin, afford no electrochemical protection to iron against corrosion attack, and that since the alloy layer is always extremely thin, the possibility of the mechanical properties of the coating being adversely affected is a very remote one

The photomicrograph in Figure 72 of tin scruff has an iron content of 2 95 per cent and shows the compound $FeSn_2$ occurring as nodules embedded in a soft matrix which is nearly pure tin The photomicrograph is illustrative of the appearance of the tin-iron alloys from 81 to 100 per cent tin at ordinary temperatures

Investigations to date have shown that the solubility of tin in iron occurs only in a very limited area, as represented by gamma in the thermal equilibrium diagram The area is restricted by both temperature levels and percentages of tin At ordinary temperatures there does not seem to be evidence of solid solutions of iron in tin The addition of tin to molten iron markedly lowers the freezing point The area in which the mixed crystals of iron and tin form as a result of the cooling of the molten alloy is modified by temperature changes At 1120° up to 18 per cent tin there is no compound formation At 890° the limit is lowered to 17 per cent tin, and at 490° to 15 per cent tin Below the melting point of tin, this percentage becomes still less In the diagram two phases are given, termed delta and alpha, one existing below 768° at which point a magnetic transformation of iron occurs, and the delta

[55] Kohman and Sanborn *Ind Eng Chem*, 19 514 (1927)
[56] "Protective Metallic Coatings," New York, The Chemical Catalog Co, Inc, 1928

constituent existing above this temperature In the area represented by delta plus liquid, the delta constituent is in equilibrium with the liquid, reacting at 1120° between 18 and 41 3 per cent tin to form the compound Fe_8Sn

The liquidus curve of the alloy diagram is relatively simple, starting from the melting point of iron, 1535°, dropping with increasing content of tin along a straight line to 1120° and a tin concentration of 47 per cent From this point the curve assumes an irregular shape to the temperature level of 890° and 96 per cent tin, then continues downward
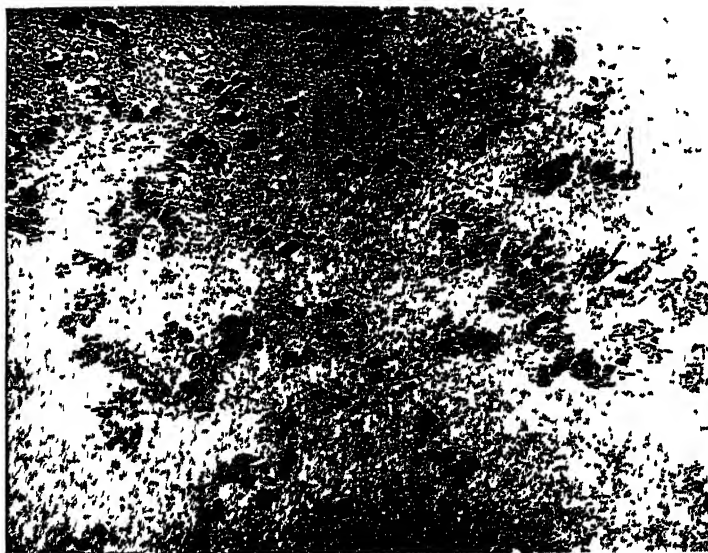
Fig 72—Photomicrograph of tin scruff
(Courtesy H S Rawdon)

to the melting point of tin, with breaks occasioned by the thermal changes of the $FeSn_2$ compound The solidus curve is quite irregular, dropping from 1535° along a curved line to 1120° and 18 per cent tin, continuing at this temperature level to 41 3 per cent tin, then dropping in a straight line to the temperature level at 890° It continues at this temperature level to 81 per cent tin, at which point the compound $FeSn_2$ is formed, dropping then in a straight line to a temperature level just below the melting point of tin, continuing at this level to 100 per cent tin

The iron-tin alloys between approximately 17 and 81 per cent tin suffer a number of constitutional changes during cooling At 890° the compound Fe_8Sn either suffers a constitutional change or reacts with

the liquid to form the solid phase delta plus the compound FeSn These mixed crystals pass through thermal changes at 780° and 755° C The delta constituent, as a result of a magnetic transformation of the iron crystals, changes at 768° to the alpha form At 755° the delta form plus the compound FeSn reacts with formation of the compound $FeSn_2$, which at 490°, as a result of thermal changes, suffers a constitutional deformation Below 490° alloys containing 15 to 81 per cent tin consist of the alpha phase, which is composed of mixed crystals of iron and tin plus crystals of the compound $FeSn_2$ in its so-called theta form, as a result of thermal changes

In tin smelting, the tin-iron alloys are known as hardheads They are obtained in a more or less pure condition in smelting operations, in the crucibles or the forehearths, or on the beds of furnaces The alloy is also formed in the tinning pots in tin-plate manufacture They form a pale to dark grey, irregularly granular or crystalline, brittle, more or less completely fused mass Hardhead generally consists of more or less metallic tin mechanically intermingled with the alloys of definite composition which appear to be chemical compounds From the thermal equilibrium diagram, it can be seen that there is only one compound which is stable at ordinary temperatures This compound, $FeSn_2$, has been carefully studied by Oudemans,[57] who has isolated it in crystals from Banka tin, and finds its specific gravity to be 7 743

The iron-tin alloys in many cases can be liquated In those containing more than two-thirds of tin, tin liquates away leaving the alloy $FeSn_2$ behind

Hardhead, as produced in smelting operations, nearly always contains arsenic Levey and Ewen [58] give the following representative analysis

	Per Cent
Sn	17 92
As	21 92
Fe	52 90
S	1 90
Insoluble	2 03
	96 67

For the occurrence of hardhead in smelting and its reworking, the reader is referred to other sections of this book

Small amounts of iron in tin markedly affect its working properties, increase its hardness, and decrease its ductility The iron-tin alloys per se have practically no industrial applications

[57] "Jaarboek van het Mijnwezen in Nederlandsch Oost Indie," 1890 I, p 24 "Over veron treiniging van Banka Tin"
[58] *Trans Am Inst Mining Met Eng*, 18 466 (1908)

Tin as an element is not found in any of the iron ores, but the use of detinned scrap may result in its introduction into steel during the process of manufacture The effect of small quantities of tin in steel has not been thoroughly investigated, but the steel maker is of the opinion that the presence of tin in steel is not to be overlooked The work which has been done shows that the tin-iron alloys have the property of making steel very hard at rolling temperatures At one works it was impossible to roll a heat of steel into which 0 75 per cent tin had accidentally been introduced Tin in steel increases the yield point and the ultimate tensile strength of the metal, but to a lesser degree than carbon or phosphorus Investigations completed at the present time indicate that 0 05 per cent tin in steel would have little influence on its mechanical or physical properties, but that larger quantities must be religiously avoided

TIN-LEAD

Tin and lead can be alloyed in all proportions The alloys were made and used by the Romans They were made by Spring[59] by strongly compressing an intimate mixture of the powdered elements, the two solids form an alloy in a few hours at 150° to 200° C.

The tin-lead system has been studied by a large number of workers The thermal equilibrium diagram is still incompletely understood, as the result of varied interpretation of the empirical results For this reason the dotted lines represent changes which the majority of investigators hold to be true, although the experimental data may be meager or capable of mixed interpretation

The liquidus curve ABC indicates a system with no compound and with the eutectic at 63 per cent tin at a temperature of 181° C

The line AD represents the final solidification of the lead-rich end for alloys from 0 to 16 per cent tin This line is drawn from Mazzotto's[60] results, which were obtained by a special method Guertler[61] embodies such a curve in his theoretical conception of the lead-tin diagram The curve is plotted with dotted lines, as other investigators have been unable to determine its shape by cooling curves or the common methods of metallographic study In the binary system of lead-antimony, which behaves analogously to the one under consideration, the corresponding solidus of the antimony in lead solid solution has

[59] *J chim Phys*, 1 593 (1903), *Bull Acad Belg*, (2), 39 548 (1875), (3), 11 355 (1886), (3), 28 23 (1894)
[60] *Intern J Metallography*, 4 273 (1913)
[61] *Metallographie*, 1911, 736

been experimentally determined with great care, and this curve is similar to the solidus AD plotted in Figure 73

The line DBE is the eutectic horizontal occurring at 181° C All alloys from 16 to 100 per cent tin become totally solid at this temperature The point E is possibly questionable, as Goebel [62] observed a solubility of 0 37 per cent lead in tin at the eutectic temperature, but all other investigators state definitely that no lead is soluble in the tin

Alloys at the temperatures and concentrations shown in the ADB area consist of a solid solution of tin in lead, and liquid Those in the area CEB are gamma tin crystals and liquid
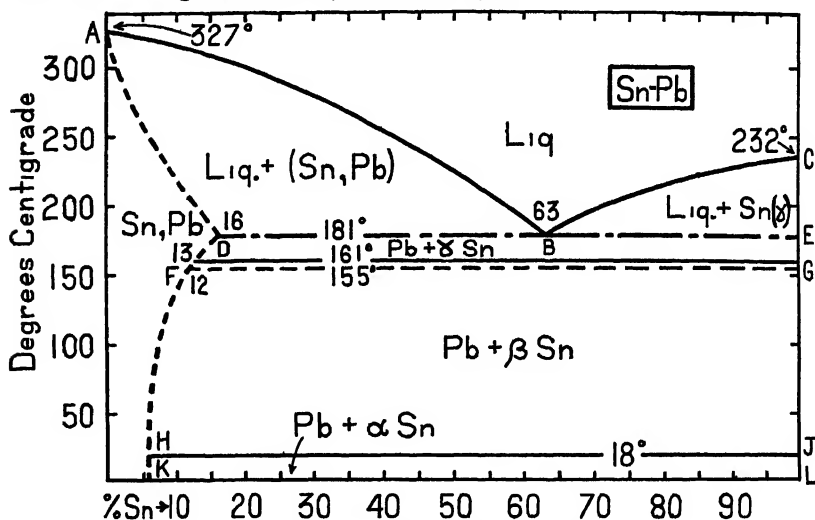
FIG 73 —Diagram of tin-lead system

The curve $DFHK$ shows the limit of solid solubility of tin in lead, and has been very carefully defined by the work of Parravano and Scorteccı. [63] They showed that solubility of tin in lead changes rapidly at the higher temperatures At 175° C the maximum solubility of tin is 14 5 per cent At 150° C the solubility is 10 0 per cent Below this temperature the curve approximates a straight line, so that the solubility of tin in lead is almost directly proportional to the temperature up to 150° C Recently this curve has been confirmed by Morgen and co-authors [64]

The area $ADFHK$ defined by the solidus AD and solid solubility curve $DFHK$ represents alloys which consist entirely of solid solution

[62] *Z Metallkunde,* 9 362 (1922)
[63] *Gass chim ital* (Roma), 50 83 (1920)
[64] Morgen, Swenson, Nix, and Roberts, *Am Inst Mining Met Eng Tech Pub* 43 (1927)

tin in lead when in equilibrium Any alloy of temperature and concentration within this area would exhibit a one-phase polygonal structure under the microscope In practice, long annealings are necessary before complete equilibrium is established

The dotted line *FG* illustrates a transformation which is generally believed due to an allotropic change of gamma tin, which is stable above the temperatures indicated by the horizontal at 155° C, to the beta form of tin, which is stable below 155° C This change is capable of variable interpretation and even its location is disputable Rosenhain and Tucker [64a] found, by dilatometric measurements, its position to be a horizontal at 161° C

A further alternative explanation of this transformation is shown at *FG* The lead constituent of the eutectic has a diminishing power of holding tin in solution This solubility decreases from 16 to 10 per cent and from 181° to 155° C *FG* may be the limit of supersaturation of tin in the cooling lead-rich solid solution, and at this temperature there may be a precipitation of the excess tin, which accounts for the slight exothermic reaction or recalescence observed on cooling

The line *HJ* represents a further transformation corresponding to the allotropic form of beta tin capable of existence above 18° C, but changes to the gray tin below that temperature

Alloys represented in the area *FHJG* consist of heterogeneous mixtures of solid solution tin in lead and beta tin, and alloys in the area *HKLJ* contain mixtures of solid solutions tin in lead and the alpha form of tin.

Phoebus and Blake [65] studied alloys of lead and tin of variable concentration by X-ray methods They show a solid solution from 0 to 3 6 per cent tin in lead, which corresponds to the face-centered cubic lattice and varies in size from 4 942 to 4 931 angstrom units Alloys of 10 to 95 per cent tin exhibit mixtures of the lead and tin lattice types

Alloys between 95 and 100 per cent tin show the lattice of pure tin both in structure and size, which obviously indicates a concentration of maximum solid solubility of 5 per cent lead in tin This is contrary to the metallographic researches which contributed to the drafting of the equilibrium diagram Further X-ray data are desirable and also more evidence of adequate annealing.

The facility with which the plumber can "wipe a joint" with high-lead solders depends upon the two freezing points of the alloy, or rather

[64a] *Trans Roy Soc (London)*, 209 89 (1908)
[65] *Phys Rev*, 25 107 (1925)

the cooling through the range of solid solution of tin in lead plus liquid in the *ABDA* area of the diagram, when the pasty condition occurs

Binary lead-tin alloys shrink on freezing

Moissan and O'Farrelly [66] found that lead could be almost completely distilled from alloys in the electric furnace

Solders consist of tin and lead in various proportions, and bismuth is added when a more fusible alloy is required The commercial applications of solders are discussed in greater detail elsewhere in this volume The same holds true for pewter and bearing metals

An interesting application of tin-lead alloys is in Fahlun brilliants, used for stage jewelry This is a 40 tin-60 lead alloy, which when molten is cast into molds, facetted like cut diamonds The finished brilliants showily reflect the light from their bright white surfaces

A large number of ternary alloys containing tin and lead have been investigated Those upon which a large amount of work has been done have the following as the third constituent arsenic, antimony, bismuth, potassium, sodium, calcium, barium, copper, silver, magnesium, zinc, cadmium, mercury, aluminum, and thallium For original sources of these systems, the reader is referred to the literature index in Mellor's "Comprehensive Treatise of Inorganic and Theoretical Chemistry," Vol VII, pages 630 to 632 A large number of quaternary systems are also given

The hardening of ternary alloys, such as type metal, increases with the tin content, temperature of casting, and rate of cooling Hardening can also take place starting from the solid metal at a temperature of 180° or over These alloys can undergo tempering even at atmospheric temperature At the end of seven months an alloy which had been cast in a chill mold had undergone approximately 67 per cent of the contraction which occurred after complete annealing Dilatometric study of lead-tin alloys showed that, with 0 to 1 per cent tin, lead which had been cast in chill molds showed signs of hardening, but after annealing at about 200°, it could not be hardened from the solid state On the contrary, tin containing a few tenths per cent lead can be hardened from the solid state The degree of hardening of lead-tin alloys increases with the tin content to a maximum at 16 per cent The dilatometric curves obtained on cooling pure lead showed one or two breaks indicating allotropic modifications In studying the transformation rhombohedral Sn $\rightleftarrows$ quadratic Sn, the calorimetric curves exhibited a discontinuity (break or flattening) at about 171-2°, when the molten tin had been overheated several hours at or above 500° No satisfactory

explanation of this anomaly has yet been found, but it may be related in some way to the allotropic transformation of tin

TIN-LITHIUM

The tin-lithium compounds are of scientific interest only, finding no uses at the present in industry Masing and Tammann [67] showed that three compounds are formed, Li_4Sn, Li_3Sn_2, and an unstable material, Li_2Sn_5, which reacts with the melt
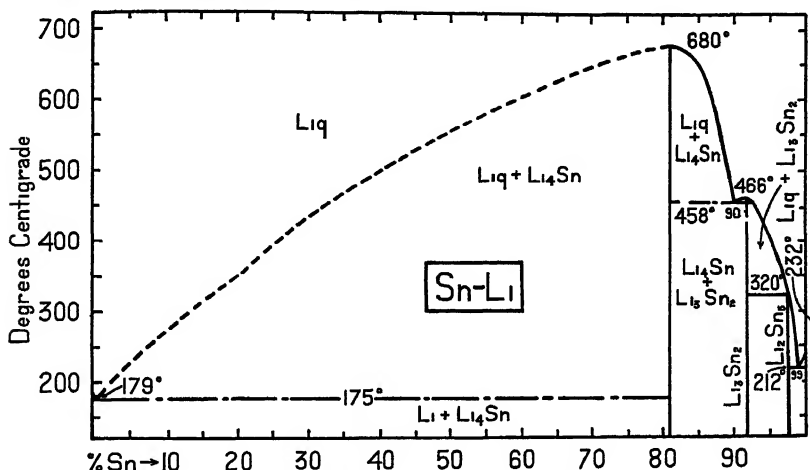
FIG 74—Diagram of tin-lithium system

The thermal equilibrium diagram is shown in Figure 74 Tin lowers the melting point of lithium four degrees to a eutectic at 175° C The liquidus curve is assumed to rise to the maximum at 680° C, the melting point of the Li_4Sn compound The liquidus then drops to the eutectic at 458° C. at 90 per cent tin The eutectic constituents are the compounds Li_4Sn and Li_3Sn_2 From the eutectic the liquidus rises to 466° C, the melting point of Li_3Sn_2, to drop rapidly to 212° C at 99 per cent tin, the eutectic between Li_3Sn_2 and tin The liquidus curve is broken slightly at 320° C due to the formation of the unstable compound Li_2Sn_5.

The tin-lithium alloys are readily corroded They react with water, the lithium being attacked to leave a tin skeleton They are all white and silvery in color They oxidize readily and are attacked by most chemical reagents

[67] *Z anorg Chem*, 67 183 (1910)

TIN

TIN-MAGNESIUM

Magnesium seems to be soluble only in a very small amount in tin, but tin is soluble to the extent of about 6 per cent in magnesium The thermal equilibrium diagram is given in Figure 75 It is of a simple eutectoid type The liquidus curve, starting at 651° C, the melting point of magnesium, gradually falls to the eutectic at 565° C, containing 39 per cent magnesium The constituents of the eutectic are magnesium and the compound $SnMg_2$ The freezing-point curve rises from the eutectic to 783° C, the melting point of the compound $SnMg_2$ (71%

FIG 75—Diagram of tin-magnesium system

tin, 29% magnesium) From here the curve drops rapidly to a eutectic at 210° C, a point corresponding to 2 3 per cent magnesium and 97 7 per cent tin The constituents of this eutectic are the compound $SnMg_2$ and pure tin From the eutectic, the freezing-point curve rises to the melting point of pure tin The compound $SnMg_2$ crystallizes well, is brittle, and readily tarnishes in air

The solidus curve drops from 651° C to a point located by the solidus line at 565° C and 9 7 per cent tin All alloys between 9 7 and 71 per cent tin finally become entirely solid at 565° C and consist of mixtures of alpha (solid solution of tin in magnesium) and beta (compound $SnMg_2$) Between 71 and 97 7 per cent tin, the solidus line is at 210° C, at which point all the alloys in this range freeze entirely, becoming mixtures of beta (compound $SnMg_2$) and tin The com-

pound beta exists alone without admixture over a very narrow and small area It has a well marked octahedral cleavage which makes the alloys brittle

Phipson [68] claimed that the alloy with 85 per cent tin 15 per cent magnesium was lavendar blue It decomposed water at ordinary temperatures Beck [69] states that the molten alloy containing 50 per cent tin absorbs 40 per cent of nitrogen Borchers and Beck [70] recommended it for obtaining nitrogen from the air

The tin-magnesium alloys in some ways have properties similar to those of tin and aluminum Their industrial use is very small and limited They have no special advantages which are not as readily obtained by alloying agents cheaper than tin

TIN-MANGANESE

Williams [71] states that the compounds $SnMn_4$, $SnMn_2$, and $SnMn$ are formed There is complete miscibility in the liquid condition In the solid condition, mixed crystals are formed from 96 to 100 atomic percentage manganese Pushin [72] states that the alloys of 0 to 30 to 40 atomic percentage manganese are white and soft At 50 atomic percentage manganese, they are harder and porous With further increases of manganese they become brittle, reaching a maximum at 66 atomic percentage The alloys of tin and manganese containing 75 atomic percentage of the latter metal are granular in structure, very hard, and brittle

The tin-manganese system has not as yet been thoroughly confirmed At the present time the alloys do not have any industrial applications, at least in their binary forms

TIN-MERCURY

Tin and mercury unite quickly at ordinary temperatures and still more rapidly if the mercury be poured into molten tin Tin readily dissolves in mercury even in the cold, and mercury dissolves in tin Liquid tin and mercury are miscible in all proportions

The freezing-point equilibrium curves are given in Figure 76 The addition of mercury to tin lowers its freezing point but only at a relatively slow rate The curve is smooth With appreciable amounts of mercury, the alloys are liquid The curve is almost a straight line from

[68] *Proc Roy Soc (London)*, 13 217 (1864)
[69] *Metallurgie*, 5 504 (1908)
[70] German Pat (D R P) 196,323 (1906)
[71] *Z anorg Chem* 55 1 33 (1907)
[72] *J Russ Phys Chem Soc*, 39 353 99

the melting point of tin to about 120°, when it gradually bends until it reaches 40°, at which point it falls almost vertically with the temperature axis At low temperatures, the amount of tin in the saturated liquid amalgam is very small Liquid amalgams, as represented by the equilibrium curve, deposit either pure tin or tin associated with very little mercury The solid phase at 25° contains 94 per cent tin On cooling the amalgams containing 0 18 to 85 per cent tin to —34 5°, a change takes place which is accompanied by the development of heat and a diminution in volume The maximum change occurs when the amalgam contains about 50 per cent tin All amalgams containing up to 60 per cent of tin finally solidfy at —38 6° Between —34 5° and —38 5°, mixed crystals separate and expansion takes place It has not
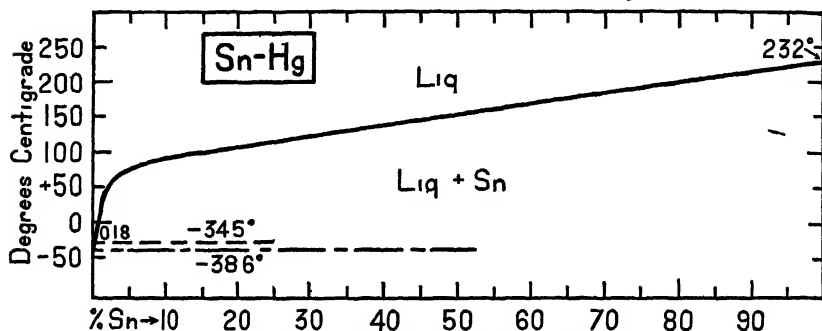
Fɪɢ 76—Diagram of tin-mercury system

been found possible to determine what modification of tin is then deposited, but its specific volume must be smaller than that of gray tin and larger than that of the ordinary variety From the study of the microstructure, there has been no evidence of the formation of chemical compounds When atomic proportions exceed Hg_4Sn, the alloys are liquid at ordinary temperatures Those with more tin than Hg_2Sn are solid The amalgam Hg_2Sn is very soft and is quite fluid at 100° If the mercury be not in excess, the color of the amalgams is that of tin Behrens [73] states that an amalgam with 10 per cent of mercury is harder than tin and can be filed When broken, the fractured structure shows six-sided prisms under the microscope Under similar conditions, a 20 per cent mercury amalgam shows octahedral crystals

The tin-mercury alloys have been largely used in the past for silvering mirrors When alloyed with a third metal in ternary systems,

[73] "Das mikroskopische Gefuge der Metalle und Legierungen," Hamburg, L Voss, 1894, p 53

they have been and are employed in dentistry (see Tin-Silver) Their industrial use is quite limited

TIN-PHOSPHORUS

The alloys of tin and phosphorus, particularly with low percentages of the second element, are quite important in commerce as the phosphor tins They find employment, along with the phosphor coppers, in the manufacture of phosphor bronzes

The system, as shown in Figure 77, is largely due to Vivian,[74] adapted by the use of the nomenclature of Haughton [75] The system has been only partially investigated, and only that portion from 0 to 50
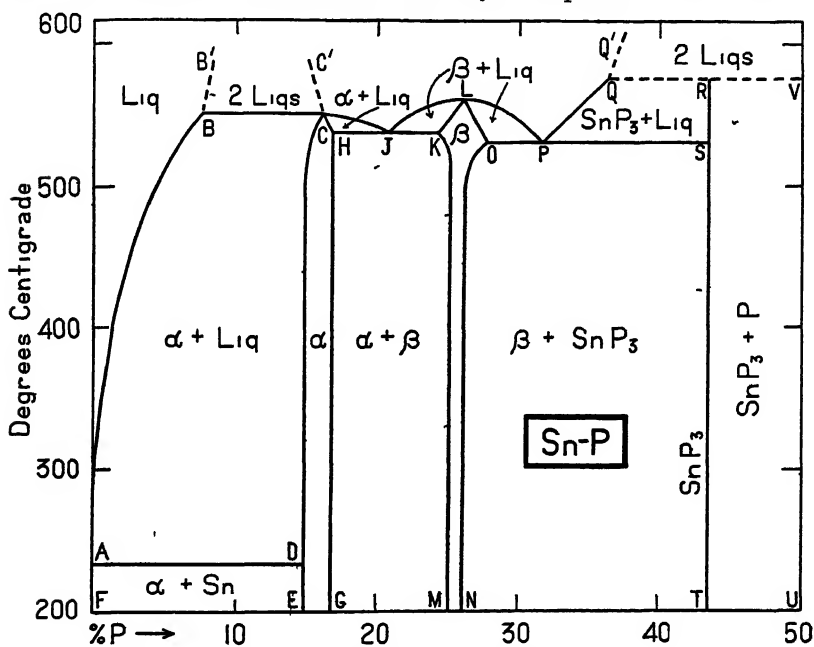
FIG 77—Diagram of tin-phosphorus system

per cent phosphorus has been studied Vivian prepared the alloys in sealed glass tubes embedded in sand in an enclosing steel case A thermocouple for temperature measurement was cemented into contact with the glass tube Up to 8 per cent phosphorus, the alloys were obtained by carefully fusing a high-percentage product at atmospheric pressure The work was attended by great experimental difficulty in the higher ranges of phosphorus, as it was found that for the formation

[74] *J Inst Metals (British)*, **23** 325 (1920)
[75] *J Inst Metals (British)*, **23** 361 (1920)

of alloys above 2 5 per cent phosphorus, the vapor phase was necessary
Pressures above atmospheric were required for alloys containing more
than 8 5 per cent phosphorus The tin-phosphorus system is noteworthy,
therefore, inasmuch as pressure is usually considered as an invariant
in thermal concentration diagrams of the metallurgical type

Vivian states that from 6 5 to 20 per cent phosphorus, conjugate
solutions occur, but between 16 and 30 per cent phosphorus there is
little sign of conjugate solutions remaining in the cooled ingot Above
30 per cent, elementary phosphorus appears, but conjugate solutions are
roughly indicated at high temperatures Up to about 12 per cent phos-
phorus the ground mass contains 14 7 per cent phosphorus, which
represents the maximum solid solution (alpha$_1$) of tin in Sn$_4$P$_3$
(alpha$_2$) The alpha-beta eutectic contains 20 5 per cent phosphorus,
and freezes at 540° The beta phosphide contains 25 8 per cent phos-
phorus, corresponding to Sn$_8$P$_4$ Above 26 per cent phosphorus, the
gamma phosphide (about 44% phosphorus) occurs as black strings
The beta-gamma eutectic contains about 31 3 per cent phosphorus and
freezes at 530° Above 44 per cent phosphorus, the alloys contain red
phosphorus The vapor phase is necessary for the formation of alloys
above 2 5 per cent phosphorus The tin arrest decreases with the phos-
phorus content to nil at 14 5 per cent From the data obtained, a tem-
erature concentration diagram up to 50 per cent phosphorus is suggested

Cowan, Hiers, and Edwards, in the American Society of Steel
Treating "Handbook of Alloys," give the most up-to-date and accept-
able description of the system

It has been suggested that the diagram as shown may be regarded
as a sloping section cut through a three-dimensional model having three
variables concentration, temperature, and pressure However, as the
pressures used were not measured and necessarily varied in the different
experiments, no definite section or plane can be considered The investi-
gator felt it advisable to reject the view of a three-dimensional model,
since the pressure functioned solely in determining the phosphorus con-
centration

With this explanation and also the mode of experimentation, the
diagram to be described must not in any way be regarded as final
Haughton's nomenclature has been adopted in discussing this work,
as his diagram attempts a provisional representation of equilibrium
conditions which is in keeping with phase rule requirements

Alloys from the tin end of the diagram begin to solidify along the
liquidus *AB* which mounts almost vertically up to 400° C , then slopes
to 550° for a phosphorus content of 8 5 per cent, shown at the point *B*

From theoretical considerations, Haughton shows the eutectic contain-
ing a minute quantity of phosphorus, but as this quantity is unknown
and so small, it is difficult to show on a diagram of the size plotted
Further work may establish the existence of the eutectic, but the cooling
curves of Vivian certainly did not show it, and for practical purposes
its consideration can be rejected

Alloys between B and C, from 8 5 to about 15 5 per cent phos-
phorus, form two immiscible liquids at about 550° C Dotted lines
BB' and CC' illustrate in a limited way the concentrations and tempera-
tures at which the conjugate solutions may exist Somewhere just above
600° it is probable that the lines BB' and CC' join, and the liquids of
these compositions are mutually soluble, one liquid phase only being
present The line BC is the liquidus for alloys of the above concentra-
tions Therefore the area bounded by the liquidus curve ABC and the
solidus AD, which is the horizontal at 232° C and the almost vertical
solidus DC, contains the alpha solid solution plus liquid Below the
solidus AD the alloy consists of pure tin and alpha solid solution

The area $EDCHG$ denotes the limits of the alpha solid solution,
E indicates 14 7 and G 16 3 per cent phosphorus The nomenclature
adopted in this area is Haughton's interpretation of the experimental
results obtained by Vivian, and the line HG shows the maximum solu-
bility of tin in the compound Sn_4P_8 Vivian's notation in this area is
confusing and does not fulfill phase rule conditions

The area CHJ represents two phases, alpha solid solution and liquid
metal The liquidus line CJ meets the solidus CHJ at the first definite
eutectic point J at 20 per cent phosphorus Alloys of increasing phos-
phorus content begin to freeze along an ascending liquidus JL to the
maximum temperature at L, the point of total freezing for a single
concentration of the beta solid solution The point L may justifiably be
regarded as the compound Sn_3P_4 from its mode of freezing, but more
experimental data will prove or disprove such a hypothesis The solidus
of alloys of concentrations between C and L is shown by the line CH,
eutectic horizontal HJK, and line KL The area JKL represents the
existence of two phases beta solid solution, which is a probable solid
solution of tin in Sn_3P_4, and liquid metal

The beta solid solution is bounded on the one side by the solidus
KL and the line of solid solubility KM, and on the other side by the
solidus LO and line of solid solubility ON Vivian's results show a pos-
sible junction of solid solubility lines KM and ON at about 440°, but
for theoretical requirements it is necessary to show a solid solution as
an area and not as a line of invariant concentration

Alloys in the area *GHJKM* consist of the alpha solid solution plus beta solid solution

The area *LOP* denotes mixtures of beta solid solution plus liquid The liquidus *LP* intersects the solidus *LOP* at the second eutectic *P*

Proceeding to higher compositions of phosphorus, the liquidus rises to the point *Q* at 580° C and then supposedly proceeds along the horizontal *QRV*

Alloys of composition *Q* and of increasing phosphorus content are believed to form conjugate solutions above 580° C The line of liquid miscibility *QQ'* is drawn dotted to indicate this probability

At about 43 per cent phosphorus and at 580°, a compound which would have a formula SnP_3 appears, and the line *RST* denotes its concentration Alloys in the area *ONTSP* consist of two phases the beta solid solution plus the compound SnP_3

Concentrations of phosphorus greater than 43 per cent indicate the existence in the solid state of the compound SnP_3 and elemental red phosphorus, but such mixtures have received little study

Commercially the tin-phosphorus alloys of low concentration are ordinarily formed by causing stick phosphorus, held in a graphite phosphorizer, to dissolve in molten tin

TIN-PLATINUM

Upon the addition of platinum to tin, according to Podkopaev [76] the fusion point of tin is gradually lowered, reaching a minimum at the eutectic point of 224° C, corresponding to 2 per cent platinum Further additions of platinum cause a quick rise in the melting-point curve which reaches a maximum at 1324° C This corresponds to 50 per cent atomic weight of platinum The curve then drops to a eutectic point of 1065° C, corresponding to 59 atomic percentage platinum, then again quickly rises to 75 atomic percentage platinum, corresponding to the compound $SnPt_3$ at 1400° C The melting point curve then continues upward to the melting point of pure platinum Tin definitely lowers the freezing point of platinum

Alloys rich in tin—that is, up to about 5 per cent atomic weight of platinum—are very soft With increase of platinum up to about 50 per cent, they become microcrystalline and brittle The compound SnPt is extremely brittle When fractured it shows shiny shell-like or conchoidal faces With further increases of platinum up to 60 to 75 atomic percentage, the brittleness decreases Still further additions of platinum cause the alloys to become tougher and more tenacious

[76] *J Russ Chem Soc* 40 249 60 (1908)

Doerinckel [77] states that there are only two compounds in the system completely defined by formulæ, $SnPt_3$ and SnPt He assigns probable formulæ to others, $SnPt_2$ and Sn_3Pt_3, but finds that most of these so-called compounds decompose during melting Only the SnPt compound melts unchanged

The alloys are of little industrial importance Tin is ordinarily a deleterious constituent of platinum in its commercial applications
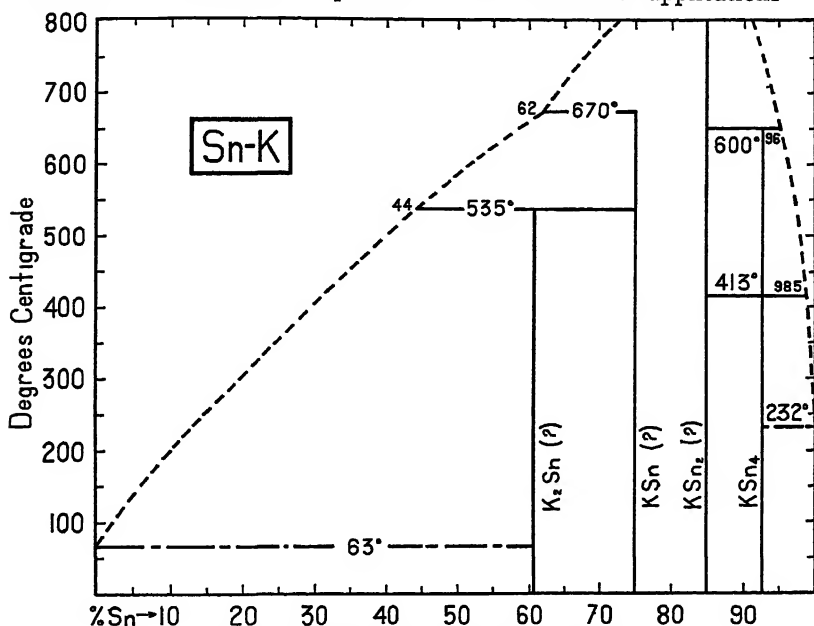
FIG 78 —Diagram of tin-potassium system

TIN-POTASSIUM

Gay Lussac and Thénard [78] found that a mixture of 7 volumes of tin filings to 2 volumes of potassium united with slight incandescence A fusible brittle alloy was formed The material had a fine-grained structure, oxidized quickly in air, and decomposed water When larger proportions of potassium were employed, the alloy took fire when heated in air A number of investigators have found that the tin-potassium alloys are pyrophoric and liberate hydrogen from water Tin and potassium are stated to be miscible in all proportions in the fused state The system is a little unusual in that most of the alloys melt at temperatures higher than the melting points of the original constituents

The thermal equilibrium diagram is given in Figure 78, but inas-

[77] *Z anorg Chem*, 54 333-66 (1907)
[78] *Metall Ers*, (2), 1 40 (1816)

much as a considerable portion of the system is as yet unconfirmed in an authoritative manner, the liquidus curve is represented by dotted lines The alloys rapidly attack glass and even steel The results of the thermal analysis, therefore, are not very conclusive The addition of tin to potassium or of potassium to tin raises the melting point of the solvent metal Starting from the potassium side, the addition of tin to potassium, melting at 63° C , causes a rise of the liquidus curve at a rapid rate to a break at a point indicated by the cross-section of the thermal-level line of 535° and 44 per cent tin The liquidus curve rises to another break at the cross-section of the thermal-level line at 670° and 62 per cent tin, due to the formation supposedly of the compound K_2Sn The liquidus curve rises further to an undetermined break at approximately 75 per cent tin, due to the formation of the compound KSn, and then to an undetermined maximum at approximately 85 per cent tin, due to the formation of the compound KSn_2 From the maximum, it drops to a break at 96 per cent tin and the temperature level of 600°, where the compound KSn_4 is formed From this break the liquidus drops directly, with a minor break at 98 5 per cent tin, to 232°, the melting point of pure tin At the present time our knowledge of the potassium-tin alloys is quite unsatisfactory Kremann and Pressfreund [79] found evidence of the compounds K_2Sn, KSn_2, KSn_4, and possibly KSn in their measurements of the electromotive behavior of the tin-potassium alloys

The tin-potassium alloys have no commercial applications but are of scientific interest Their corrosive action on ordinary materials of construction is quite marked

Tin-Silver

The tin-silver alloys are employed in making dental amalgams The binary alloy appears to undergo profound changes through the lapse of time Black [80] showed that fresh filings of tin-silver alloys require 50 per cent more mercury for amalgamation than do similar filings which have been aged for several months or heated to 100° for a half hour The aging does not occur in a bar of alloy during several weeks' heating under the same conditions where filings are aged in an hour Exclusion of air does not affect the results

Gehlen [81] observed that tin and silver combine readily without incandescence The specific gravity of the product is greater than the

[79] *Z Metallkunde*, 13 19 (1921)
[80] "A Work on Operative Dentistry," Chicago, Medico Dental Pub Co , vol 2, 1914, 309, *Dental Cosmos*, 37 353, 469, 553, 571, 637, 737 (1895), 38 43, 965, 982 (1896)
[81] *Schweigger's J ,* 20 353 (1817)

mean between the specific gravities of the constituents Alloys with silver and tin in the proportion of 2 to 1 are hard, while those in the proportion of 1 to 2 are malleable Wright [82] states that the molten elements are mutually soluble in all proportions Studies of a large number of workers have shown that if the tin-silver alloys be well annealed, the presence of only one compound, Ag_3Sn, is shown With alloys containing over 50 per cent tin, there is a solid solution of silver in Ag_3Sn The Ag_3Sn compound becomes stable below 460°
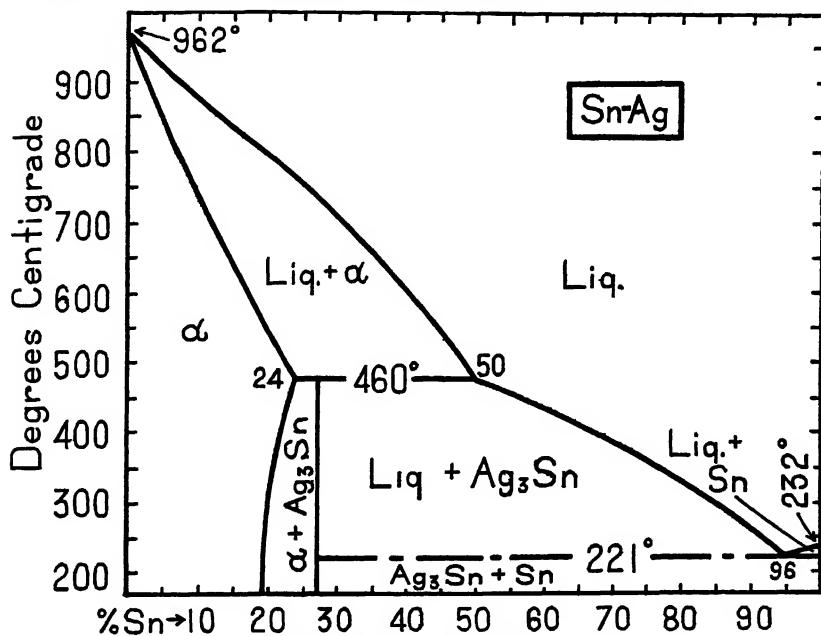
FIG 79 —Diagram of tin-silver system

The thermal equilibrium diagram for the system is given in Figure 79 The liquidus curve starts at the melting point of silver, 962°, and, with increasing percentages of tin, drops to a break at 50 per cent tin and the temperature level of 460°, continuing then to the eutectic at 96 per cent tin and 221°, and rising from there to 232°, the melting point of tin The solubility of tin in silver varies with the temperature The area alpha is a solid solution of tin in silver The solidus curve drops from 962° to the junction point of the temperature level of 460° and 24 per cent tin In the area between the solidus and the liquidus at this point, the solid solution of tin in silver is in equilibrium with the

[82] *J Soc Chem Ind*, 13 1016 (1894).

molten metal From approximately 19 to 27 per cent tin and between
the temperatures of 460° and room temperature, the solid alloy consists
of a mixture of a solid solution of tin in silver and the compound
Ag_3Sn Between 27 and 96 per cent tin and 460° and room temperature,
the area represented between the temperature levels of 460° and 221°
shows the compound Ag_3Sn in equilibrium with the molten alloy As a
result of the reaction between the compound and the liquid, there are
formed below 221° mixed crystals of the compound Ag_3Sn plus tin
metal From 96 to 100 per cent tin, the area between the solidus line at
221° and the liquidus curve shows tin in equilibrium with the molten
alloy, reacting at 221° to form mixed crystals of the compound Ag_3Sn
plus tin

The alpha solid solution is characterized by prolific twinning of the
crystals, accompanied by the development of finer marking following
the course of cleavage planes in the crystals The compound Ag_3Sn,
after prolonged annealing, consists of polygonal crystals with fine cross
hatch markings

In the literature, there has been considerable diversion of opinion
as to the compounds formed between silver and tin None of these,
with the exception of Ag_3Sn, has been confirmed

The commercial application of silver-tin alloys is largest in dental
work, in the manufacture of instruments, and similar usages The
applications are quite special and at no time are they consumers of
large amounts of tin or silver

TIN-SODIUM

Studies of the tin-sodium alloys show that they have properties
quite similar to the tin-potassium series Heycock and Neville [83] found
that the freezing point of tin was raised 11 61° by the addition of 4 57
atomic per cent of sodium

The thermal equilibrium diagram is given in Figure 80 It is of
the same general nature as the tin-potassium alloys The addition of
sodium to tin markedly affects the freezing point The liquidus curve
rises from 97 5°, the melting point of sodium, to a break at approxi-
mately 58 per cent tin and 405°, which is the eutectic between sodium
and the compound Na_2Sn and corresponds to the compound Na_4Sn
The liquidus rises from this eutectic to a first maximum at 470° and
72 1 per cent tin The curve then drops to a eutectic at 440°, rises to
a break at 478° and 80 per cent tin, corresponding to the compound
Na_4Sn_8, and continues to a maximum at 576°, 83 8 per cent tin, corre-

[83] *J Chem Soc*, 55 666 (1889), 57 380 (1890)

sponding to the compound NaSn From maximum the liquidus drops directly to the melting point of tin, 232°, with breaks at 478° and 305° The compound Na_4Sn above 405°, being in equilibrium with the molten alloy, undergoes transformation at 405° with the formation of the compound Na_2Sn and fused alloy   The compound Na_4Sn_8 is the hardest
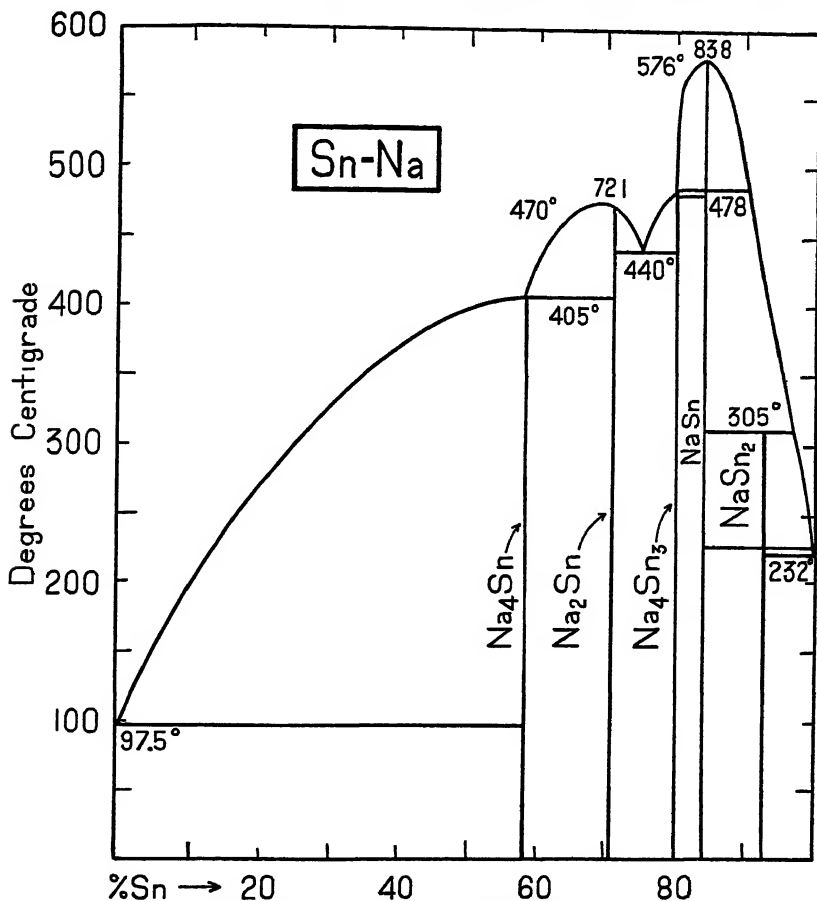
FIG 80 —Diagram of tin-sodium system

and most brittle of the five formed   At 478° it melts with a transformation into NaSn plus fused alloy The compound NaSn, with a melting point of 576°, undergoes a polymorphic transformation at 483°, according to the data of C H Mathewson [84] The compound $NaSn_2$ is the softest and toughest of all This material, as well as NaSn, looks the

[84] *Z anorg Chem*, 46 94 (1905)

same as tin metal Mathewson states that a freshly cut surface of the Na_4Sn or the Na_2Sn alloy soon becomes covered in the air with a bronze film When protected by oil, the surface of the Na_2Sn compound resembles that of tin, while the color of the Na_1Sn material is steel blue The Na_4Sn_8 compound shows a pale blue color on a freshly cut surface Kremann and Gmachl-Pammer [85] found that the electrical conductivity curve showed singular points corresponding with Na_4Sn, Na_2Sn, $NaSn$, and $NaSn_2$

Because of their lack of commercial application, as well as the extreme difficulty in studying this system, many of the compounds in the curves are in doubt

Tin-Strontium

The alloys of tin and strontium have been little studied They are difficult to prepare as a result of the rapid oxidation of the strontium metal under ordinary atmospheric influences Even with protective layers of fluxes, considerable metal is lost With appreciable percentages of strontium, they are decomposed by water, leaving a tin skeleton They are of no industrial importance at the present time

The tin-strontium system has not been thoroughly investigated It is stated that the alloys are similar to those of tin and calcium

Tin-Tellurium

Tin and tellurium unite to form the compound SnTe which, according to Fay,[86] melts undecomposed at 769° This compound forms a eutectic with tellurium, as shown in the thermal equilibrium diagram in Figure 81, which contains 85 per cent tellurium melting at 399° C The compound SnTe also forms a eutectic with tin of exceedingly low tellurium concentration

The tin-tellurium system has been little studied, partly because of the experimental difficulty in making alloys of high tellurium content Tin and tellurium unite with the evolution of considerable heat

The solubility of SnTe in tin is exceedingly low and is as yet undetermined The tin-tellurium alloys are not of industrial importance, inasmuch as they find practically no commercial applications They are, however, of some scientific interest

Tin-Thallium

The effect of thallium on the melting point of tin has been studied by a number of workers In its essentials, the thermal diagram, as shown

[85] *Z Metallkunde,* 12 257 (1920)
[86] *J Am Chem Soc,* 29 1265 (1907)
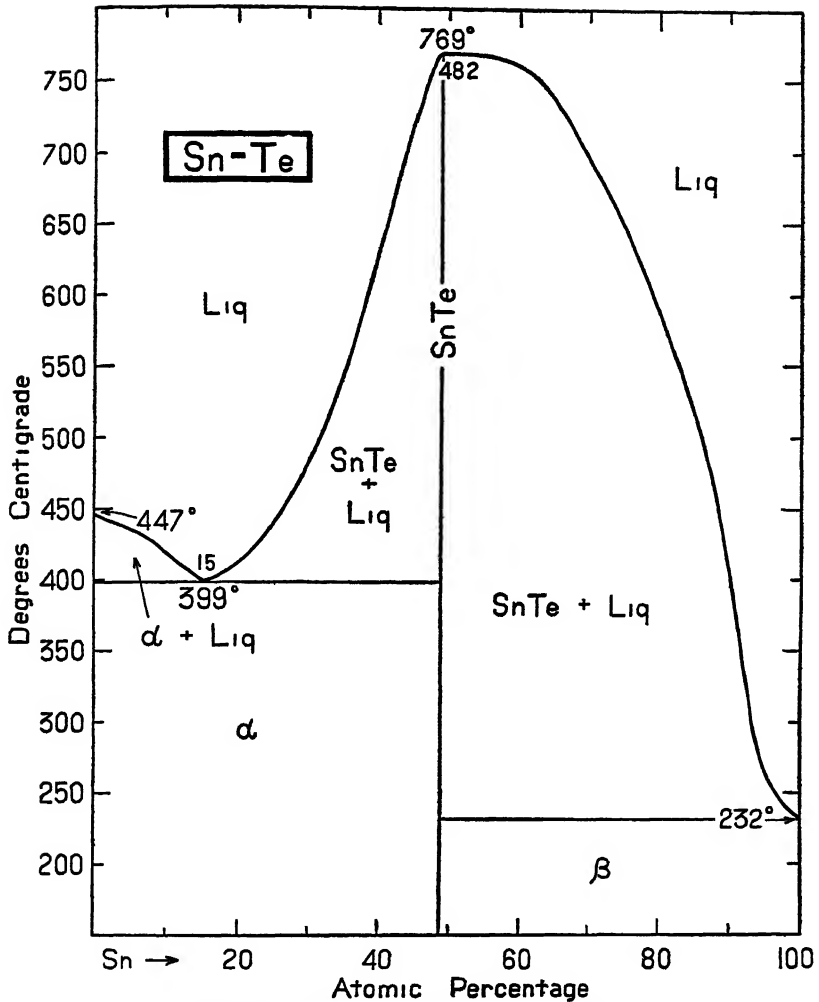
FIG 81—Diagram of tin-tellurium system

in Figure 82, is one of simple solution of the metals in each other, with but one eutectic and no compound formation The diagram is made more complex by the transitions of thallium metal

The tin-thallium alloys are fusible and ductile The eutectic occurs at 42 5 per cent thallium, at a melting point of 167° C Thallium markedly lowers the freezing point of tin The eutectic line extends from 0 to 80 per cent thallium Tin-thallium alloys with less than 80 per cent of thallium show a second arrest on cooling, in addition to the arrest
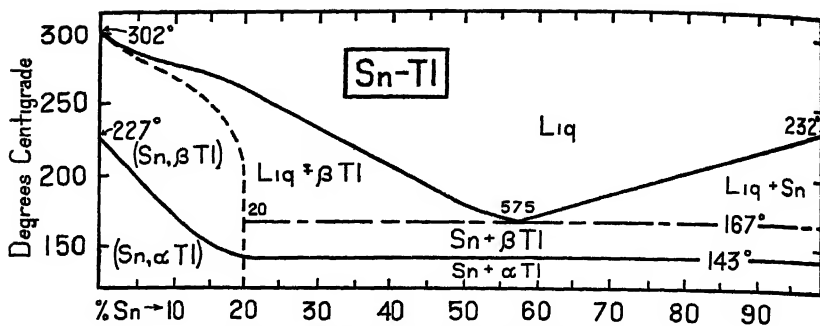
Fig 82 —Diagram of tin-thallium system

point at the eutectic tempeiature, at 143° C This aiiest iepresents the transition point of thallium, lowered through the influence of tin, from about 227° C In the solid solution iegion, from 80 to 100 per cent thallium, the transition point is lowered according to the amount of tin present

Electromotive force measurements of the alloys show no signs of compound formation Omodei [87] gives the melting point of a 30 per cent thallium alloy as 186° C , a specific gravity of 7 786 when molten, and 8 054 when solid It has a high coefficient of thermal expansion, being 0 0001184.

The Tl-Sn-Bi system has been studied by Carstanjen [88]
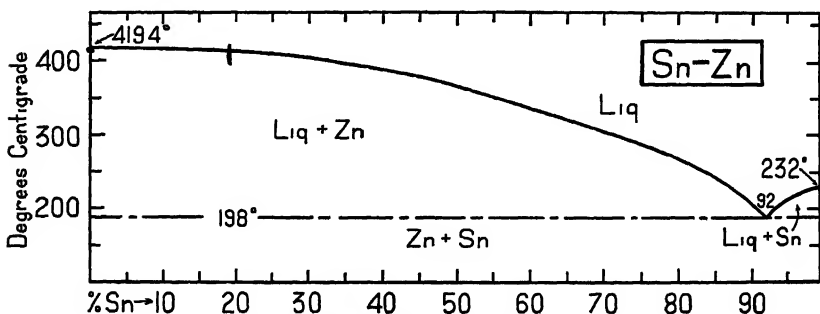
Fig 83 —Diagram of tin-zinc system

TIN-ZINC

The tin-zinc alloys are readily formed by melting together mixtures of the metals A large number of workers in the field have shown that the two metals are mutually soluble in all proportions in the fluid state The system, as shown in Figure 83, is of the simple eutectic type There

[87] *Atti accad Fisico critici siena* (4) 2 515 (1890)
[88] *J prakt Chem* (1), 102 83 (1867)

is no evidence of solid solubility on the zinc side There is definite evidence that if zinc holds any tin in solid solution, the limit is less than 0 05 per cent The data of Fuchs [89] and Endo [90] indicate that the limit of solid solubility of zinc in tin is not over 0 03 or 0 05 per cent zinc by weight The eutectic temperature is 198° C The eutectic itself has a tin concentration of 92 1 per cent, with 7 9 per cent zinc Alloys up to 92 1 per cent tin, therefore, contain primary zinc crystals and the eutectic The surface tension between the eutectic and the zinc crystals is low The eutectic, therefore, even when present in very small amounts (even less than 0 05% tin), forms extensive thin intercrystalline films These are exceedingly brittle and are ordinarily considered to be a cause of hot shortness, because of their low melting point

J W Richards [91] suggested that the alloy in the proportions of Sn_4Zn_3 would be useful as a solder for aluminum Habermann [92] recommended the alloy with 83 per cent zinc for the production of hydrogen from acids Lambert [93] used an alloy of tin, zinc, and antimony as an aluminum solder

A number of ternary systems have been studied, that of Sn-Zn-Bi by Muzaffar,[94] and the Sn-Zn-Cu system by Hoyt,[95] Reason,[96] Guillet,[97] Hudson and Jones,[98] and Tammann and Hansen,[99] the Sn-Zn-Sb system by Campbell,[100] and the Zn-Sn-Bi by Wright [101] and Campbell [100]

Vicentini [102] found that the microstructure of the alloys of tin and zinc is difficult to interpret due to the tendency of the alloys to liquate

TIN-ZIRCONIUM

J. W. Marden and M. N Rich [103] were unable to make a zirconium-tin alloy directly H S Cooper [104] made pyrophoric alloys of zirconium and 20 to 40 per cent tin

The tin-zirconium system has been little investigated The commercial applications and possible uses of the alloys are only minor and on an exceedingly small basis

[89] *Z anorg Chem*, 109 80-88 (1920)
[90] *Sci Rep Tôhoku Imp Univ*, 14 Series 1, 479 512 (1925)
[91] *J Franklin Inst*, 140 351 (1895)
[92] *Z anal Chem*, 28 88 (1889)
[93] U S Pat 906,637 (1908)
[94] *J Chem Soc*, 123 2341 (1923)
[95] *J Inst Metals*, 10 235 (1913), 14 178 (1915)
[96] *Metal Ind*, 12 325 (1918)
[97] *Rev Met*, 18 445 (1921)
[98] *J Inst Metals*, 14 98 (1915)
[99] *Z anorg Chem*, 138 137 (1924)
[100] *J Franklin Inst*, 154 1, 131, 201 (1902), *J Am Chem Soc*, 26 1312 (1904)
[101] *J Soc Chem Ind*, 13 1016 (1894), *Proc Roy Soc (London)*, 48 25 (1890), 50 372 (1891), 52 11 (1892)
[102] *Atti accad lincei*, (5), 1 383 (1892)
[103] "Investigations of Zirconium with Especial Reference to the Metal and the Oxide," *Bur Mines Bull*, 186 (1921), *J Ind Eng Chem*, 12 651 (1920)
[104] *Trans Am Electrochem Soc*, 43 209 (1923)

TABLE 8

A List of Alloys Containing Tin *

Bronzes

	Cu	Sn	Zn	Pb	P	Other Elements
Acid Bronze	82 00	8 00	2 00	8 00		
Argozoil	54	2	28 00	2		Ni, 14 0
Bearing Bronze (Kaiser)						
Locomotive	74	10	9	7		
Prussian	84	15	1			
French (Northern)	82	10	8			
Russian	77	10 2	5 1	7 7		
Railroad Cars	75	20	5			
Rheinland	86	12	2			
E B D , Breslau	88	10	2			5% of PSn added
Automobile	78	8	1	12		1% of PSn added
Various	83	14	2	1		
	83 7	14 2	2 1			
	85 5	12 8	1 7			
	83	12	5			
	85	11	4			
	74 5	9 5	8 9	7 1		
	77	9	14			
	83 7	8 8	7 5			
	81	7	3	9		
	87 5	8 12	2 5	1 87		
	86	6	5			Mn, 2 7
	75	4	21			
Bearings of Engines	79	8	5 0	8 0		
Bell Metal						
Old Bell at Rouen	71	26	1 8	1 2		
Herbohn	60	35	5 0			
Herbohn	71 43	26 4	2 7			
Karakane	65 95	17 25	3 45	10 35		
Karakane	64	24	9			Fe, 3 0
Karakane	62 5	25	9 4			Fe, 3 1
Karakane	61	18	6	12		Fe, 3 0
Bismuth Bronze	53	15	20			Ni, 10 , Al, 1, Bi, 1
Brasses	74 4	9 5	8 9	7 1		
Brasses	70	10	10	10		
Brasses	74	1 0	10	15		
Bridge Bronze	88	10	2		0 25	
Bushings	86 2	10 2	3 6			
Bushings	85	11	4			
Camelia	70 4	4 2	10 2	14 7		Fe, 0 5
Carbon	75 4	9 7		14 5		
Carriage Wheel Bearing	84	16				
Chinese	74	1 0	10	15		
Cocks	88	10–8	2–4			
Cogs and Worms	85	11	4			
Coinage	95	4	1			
Cooper's Speculum	57 8	27 3	3 6			As, 1 2, Pt, 10
Damascus	77	10 5		12 5		
Damar	76 4	10 6		12 5		
Daimler Bearing	76	3	20	1		

* From Campbell's List of Alloys, *Proc Am Soc Testing Materials*, 1922

TABLE 8—*Continued*

	Cu	Sn	Zn	Pb	P	Other Elements
Dudley's B	77	8		15		
Dudley's K	77	10 5		12 5		
Dudley's Phosphor	79 7	10		9 6	0 8	
Durena	65	2	30			Al, 1 5, Fe, 1 5
Dysoid	62	10	10	18		
Edward's Speculum	63 3	32 2				As, 1 6
Edward's Speculum	69 8	25 1	2 6			As, 2 4
Eisen-Bronze	82 5	8 55	4 45			Fe, 3 95
Eislers	94 1	5 9				
Eccentric Ring	84	14	2			
File Bronze	64 4	18	10	7 6		
File Metal (Genfer)	64 4	18	10	7 6		
File Metal (Genfer)	62	20	10	8		
File Metal	60 89	30 69		8 42		
File Metal	54 54	30 48	7 49	7 48		
Flange Metal (German)	92 4	2 5	5 05			
Flange Metal (French)	94 35	5 6		0 05		
Gearing	91 3	8 7				
Gear Bronze	88	10			2	
Gear Bronze	85	13	2			
Gears	85	10	3	2		
Gun Metal	90	10				
French, Modern	90 1	9 9				
French, Old	89 44	8 91	1 39	0 16		
Prussian, Modern	90 9	9 1				
English, Modern	89 3	10 7				
English, Modern	91 74	8 26				
Russian, Modern	90 8	9 2				
Russian, 1813	88 61	10 7				Fe, 0 69
Swiss (Lucern)	88 93	10 37	0 42			
Cochin China	77 18	3 42	5 02	13 22		Fe, 1 16
Cochin China	93 19	5 43				Fe, 1 38
Chinese, 1901	93 2	5 05				Fe, 1 72
Turkish, 1464	95 2	4 31				
Turkish, 1907	90 9	8 8				Fe, 0 2
Gun Mount	80	3	17			
Graney Bronze (Law)	75 8	9 2	15			
Gurney's	75 8	9 2	15			
Hercules	85 5	10	2			Al, 2 5
High Temperature	89 8	2 67	6 24	1 29		
Hydraulic	83 0	10 8	6 0	0 1		
Instrument	82	13	5			
Instrument	82 1	12 8	5 1			
Johnson Locomotive Bearing	87 5	7 85	5 07			
Kern's Hydraulic	78	12	10			
Kochlin's Bearing	90	10				
Kuhne Phosphor Bronze	78	10 6		10 45	0 57	Ni, 0 26
Lafond's Bronze	83	15	1 5	0 5		
Lafond's Axle Bearing	80	18	2			
Lafond's Straps	84	14	2			
Lafond's Pumps	88	10	2			
Lafond's Heavy Bearing	83	15	1 5	0 5		
Lafond's Malleable	98 04	1 96				
Lowroff Phosphor Bronze	70	13		16	1	
Lowroff Phosphor Bronze	90	4		5 5	0 5	

TABLE 8—*Continued*

	Cu	Sn	Zn	Pb	P	Other Elements
Laderig's Speculum	69	28 7				
Medal	92	8				
Medal	97	1	2			
McKechnie's	56 71	40 79	1	0 5		Fe, 1
Manheim Gold	83 7	7	9 3			5% Phos Tin added
Manganese Bronze	82	8	5	3		Mn, 2 0
Manganese Bronze	83 5	8	5	3		Mn, 0 5
Mudge's Speculum	68 82	31 18				
Needle	84 5	8	5 5	2		
Nongran	87	11	2			
Neogen	58	2	27			{ Ni, 12, Al, 0 5, Bi, 0 5
Naval Gun Metal G	88	10	2			
Naval Journal, H	83	13 5	3 5			
Naval Journal, HX	83	13 5		3 5		
Naval Valve, M	87	7	6			
Naval Phosphor, Cast	88 89	8 08	2 52		0 5	
Naval Phosphor, Rolled	95	4 5			0 5	
Oil Cups	87 62	5 15	7 22			
Oil Pump	84 69	3 06	9 19		3 06	
Ounce Metal	85	5	5	5		
Ormulu	59 18	17 04	23 78			
Ormulu, small	94 12	5 88				
Ormulu, large	90 5	6 5	3 0			
Perking Brass	76 2	23 8				
Perking Brass	80	19 82	0 14			
Phosphor Bronze						
Wire	98 75	1 2			0 05	
Hard	92 8	7			0 2	
Very Hard	80	9			1 0	
Rolling	95 6	4 5			0 1	
Charpy	87 18	12 41			0 4	
Charpy	85 95	13 58			0 47	
Law	88 12	10 87			1 01	
Law	89 68	9 61			0 71	
Bridge	79 2	19 8			1–0 2	
Bridge	84 15	14 85			1	
Bearings	82 17	13 85	1 98	1	1	
Bushings	79	10		10	0 7	
Gears	88	10		2	0 1	
Gears	85	13	2		0 1	
Gears	79 92	12 3		7 68	0 1	
English	79 2	10 2		9 6	0 97	
Pennsylvania Railroad	79 7	10		9 5	0 8	
Pennsylvania Railroad "B"	76 8	8		15	0 2	
Pennsylvania Railroad "B"	85 55	9 85	3 77	0 62	0 05	
Pennsylvania Railroad "B"	80	8		10		2% of Phos Tin
Russian	93 7	5 8	0 34		0 17	
Piston Rings	84	2 9	8 3	4 3		
Piston	83	1	16			
Railroad (Hughes)						
Slide Valves	84 5	10		5	0 5	
Injector	84	8 5	5	2 5		
Phosphor Bronze	89 39	10 1			0 51	

TABLE 8—*Continued*

	Cu	Sn	Zn	Pb	P	Other Elements
Axle Box Bearing	80	5		15		
20-Ton Wagon	70 59	5 88		23 53		
Railroad (Thurston)						
Axle Bearings, French	82	10	8			
Axle Bearings, Common French	78	20	2			
Axle Bearings, Lafond	80	18	2			
Axle Bearings, Hard	87 05	7 88	5 07			
Eccentric Strap, Dutch	85 25	12 75	2 0			
Eccentric Strap, Lafond	84	14	2 0			
Gearing	88 8	8 5	2 7			
Locomotive Bearings	89	2 4	7 8			Fe, 0 8
Locomotive, Durable	73 14	9 45	9 45	7 46		Fe, 0 5
Pistons and Rods	74 1	3 7	22 2			
Richardson's Speculum	65 3	30	0 7			As, 2 0, Si, 2
Roman Bronze	90	9				
Ross' Alloy	68 2	31 8				
Sallit's Speculum	64 6	31 3				Ni, 4 1
Sheet Bronze	90	10				
Sheet Phosphor	94 5	5 0				0 5% Phos Tin
Sheet Phosphor	95	4				1.0% Phos Tin
Sashchain	92	8				
Sashchain	95	5				
Screw-Nut	86	11 4	2 3			
Slide Valve	88 5	2 5	9			
Steam Fittings	88	8	2	2		
Silicon Bronze	98 55	1 45				Si, 0 05
Silicon Bronze	91	9				Si, 0 05
Statuary Bronze						
Column Vendome	89 2	10 2	0 5	0 1		
Column of July, Paris	91 4	1 6	5 6	1 4		
Napoleon I, Paris	75 0	3 0	20	2 0		
Henry IV, Paris	89 62	5 7	4 2	0 48		
Louis XIV, Paris (1699)	91 4	1 7	5 53	1 37		
The Shepherd, Potsdam	88 68	9 2	1 28	0 77		
Bacchus, Potsdam	89 46	7 51	1 63	1 21	0 18	
Germanicus, Potsdam, 1820	89 78	6 16	2 35	1 33		Ni, 0 27
Mars and Venus, Munich	93 83	4 75	0 29	0 66		Ni, 0 48
Bavaria, Munich	91 55	1 77	5 5	1 3		
Munich	92 88	4 18	0 44	2 31	0 15	
Munich	77 03	0 91	19 12	2 29	0 12	Ni, 0 43
Augsburg	89 43	8 17	.	1 05	0 34	Ni, 0 19
Augsburg	91 27	1 58	0 52	6 01		Ni, 0 68
Grosser Kurfurst, Berlin	89 71	5 86	1 65	2 64	0 13	
Frederick the Grt, Berlin	88 3	1 4	9 5	0 7		
Melanchron, Wittenberg	89 55	2 99	7 45			
Speculum, Cu₄Sn	68 25	31 75				
Speculum, English	66 6	33 4				
Speculum, Chinese	80 8	10 7				Sb, 8 5

TABLE 8—*Continued*

	Cu	Sn	Zn	Pb	P	Other Elements
Schmidt Locomotive Bearing	86	14				
Seraing Bearing	86	14				
Seraing Piston Rings	89	2	9			
Stephenson, Locomotive Bearing	79 5	7 5	5 0	8 0		
Stephenson, Piston Rings	84	2 9	8 3	4 3		Fe, 0 4
Stone's English Gear	89	11				
Telegraph Bronze	80	5	7 5	7 5		
Tin Bronze	89	11				
Uchatius Bronze	92	8				
Valves	85	9	6			
Valve Bronze	89	5	3	3		
Valve Bronze	83	4	7	6		
Valve, Steam	88	10	2			
Weights	90	8	2			
Whistles	80	18	2			
Whistles, Lafond	81	16	2			
Whistles, Lafond	80	18				Sb, 2 0
Wire	98 75	1 2			0 05	

Brasses

	Cu	Zn	Sn	Pb	Fe	Other Elements
Admiralty, A	70	29	1			
Bell Brass	64 25	35	0 75			
Bismuth Brass	47	21	1			Ni, 30 9, Bi 0 1
Bow Wire	93	2	5			
Brush Wire	64 25	35	0 75			
Button Brass	89 50	10	0 50			
Buttons (Thurston)						
Bristol Alloy	57 9	36 8	5 3			
Bristol Alloy	61 12	36 11	2 77			
Jackson's Alloy	63 88	30 55	5 55			
Jackson's Alloy	63 01	35 61	1 39			
"Bidery"	48 50	33 32	6 06	12 15		
"Gold"	58 71	33 03	5 50	2 75		
Commercial Castings	62	30	6	2		
Diaphragm Brass	95	2	3			
Doctor Metal	88	9 50	2 50			
Durana	65	30	2		1 5	Al, 1 5
Electric Brass Castings, B E	84	13	3			
English	70 3	29 3	0 17	0 26		
Fob Metal	87 50	12	0 50			
Fourdrinier Wire	84 63	15	0 37			
Gold Leaf Jemmapes	64 6	33 7	1 4	0 2		
Gold Leaf Aix	64 8	32 8	2 0	0 4		
Guettier's Button	61 5	32	6 5			
Guettier's Button	61 4	28 9	9 7			
Hardware Bronze	88	9 50	1 50	1 0		
Harlington Bronze	55 7	42 7	0 97		0 58	
Harmonia Bronze	55 7	41 2	0 5	0 46	1 29	Al, 0 86
Iserlohn, Cast	63 7	33 5	2 5	0 3		
Jewelers Metal	91 50	6 50	2 0			
Jewelers Metal	88	11 25	0 75			
Jewelers Metal	87 50	12	0 50			
Jewelers Metal	91	7 50	1 50			

TABLE 8—*Continued*

	Cu	Zn	Sn	Pb	Fe	Other Elements
Machinery Brass	83	16	1			
Manganese Brass	60 15	34 76	0 94	0 39	1 19	Mn, 2 34, Al, 0 2
Mn Ni Brass	63 5	28 28	1 22	0 17	1 44	Mn, 3 24, Ni, 2 14
Mn Ni Brass	53 5	39	0 07		2 78	Mn, 1 52, Ni, 2 35
Mn–Bronze, Rolled	64 84	33 74	1 09			Mn, 0 33
Manganin	53 4	39	2 66			Ni, 2 5, Mn, 1 7, Al, 0 2
Manheim Gold	89 4	9 92	0 62			
Manheim Gold	83 7	9 3	7			5% of Phos Tin added
Naval Brass	61	38	1			
Oker Brass (Harz)	62 84	36 46	0 58	0 12		
Optical Bronze	89 00	6 50	4 50			
Oreide	87 25	11 50	1 25			
Oreide	80 5	14 5	4 85	0 1		
Oreide, Brunswick	68 07	31 45	0 48			
Parson's Mn Bronze	60 15	34 76	0 94	0 39	1 19	Mn, 2 34, Al, 0 23
Pen Metal	85 00	13 00	2 00			
Pewter (Thurston)						
Berthier's Alloy	71 9	24 9	1 2	2 0		
Cast and worked	63 56	34 26	0 2	1 98		
Cast and worked	61 6	35 3	0 6	2 5		
Cast gilt	63 7	33 5	2 5	0 3		
Cast gilt	64 5	32 4	0 2	2 9		
For clock work	60 66	36 88	1 35	0 74		
For clock work	64 01	33 52	1 53	0 93		
Potinjaune	71 9	24 9	1 2	2 0		
Reed Brass	69 00	30 00	1 00			
Russian, Cast	78	21	1			
Screen Plates	58 00	41 00	0 75	0 25		
Screw Bronze	93 50	5 00	1 00	0 50		
Screw Brass	78	16	4 5	1 5		
Solder (Thurston)						
Yellow, Hard	54 39	43 97	1 33	0 31		
Nearly White, Soft	44 72	50 71	3 35	1 22		
White, Very Soft	57 44	27 98	14 58			
Sheet						
Stollberg	64 8	32 8	0 4	2 0		
Jamappes	64 6	33 7	0 2	1 4		
Oker	55	44 5	0 5			
Romilly	70 1	29 26	0 17	0 28		
China	56 6	38 2	3 3	1 0	1 40	
Hegermuhl	71 73	27 28	0 2	0 79		
Hegermuhl	72	27	1			
Hegermuhl	62	37	0 5	0 5		
Hegermuhl	62	37	1			
Similor	89 4	9 93	0 6			
Similor	83 7	9 3	7 0			
Sterro Metal	55	42 4	0 83		1 8	
Talmi Gold	86 4	12 2	1 1		0 3	
Thurston's	55	44 5	0 5			
Tissier's	97	2 0	0 5			
Tobin Bronze	60	38	2			
Tobin Bronze	59	39	2			
Tombac						
Golden	82	17 5	0 5			
French	80	17	3			

TABLE 8—*Continued*

	Cu	Zn	Sn	Pb	Fe	Other Elements
Tubes, etc						
Russian	59 72	38 62	0 16	0 34	1 1	
Admiralty	70	29	1 0			
Tungsten Brass						
(N1, 0 75)	59 73	33 97	0 15			Al, 2 8, W, 2, Mn, 0 7
Wire	70 29	29 26	0 17	0 28		
Wire, English	70 29	29 36	0 28	0 17		

Nickel Silver

	Cu	Zn	N1	Fe	Sn	Pb	Other Elements
Alpakka	63 94	19 24	14 55	0 4	0 12	0 03	Ag, 2 02
American Silver, Cast	49 36	20 7	24 2	1 3	0 45		Mn, 3 83, Al, 0 13
American Silver, Cast	57 7	24 2	15 3	0 6	0 69	1 5	
Arguzoid	55 78	23 2	13 4		4 03	3 54	
Bismuth Bronze	38 79	18 53	28 02		13 79		B1, 0 86
Bismuth Bronze	53	20	10		15		B1, 1, Al, 0 1
Bismuth Brass	46 58	20 81	30 62		1		B1, 0 99
Casting	55 8	23 7	23 4		4	3 5	
Maillechort, Paris	68 52	13 88	13 88	3 32	0 23	0 16	
Neogen	58 0	27	12		2		B1, 0 5, Al, 0 5
Nickel Bronze	60	12	20		8		
Nickel Bronze	77 05		4 92		16 39		PSn, 1 6
Nickel Bronze	47	21	30 9		1		B1, 0 1
Nickel Bronze	50	18	12		2	18	
Nickel Bronze	61 5	10 95	15 35		1 88	10 15	
Nickel Bearing	50		25		25		
Seawater Bronze	45	5 5	32 5		16		B1, 1
Smitter-Lenian	72	9 75	12 75	2	2 25		B1, 1
Turbine Bushing	61 5	10 95	15 35		1 9	10 15	
Toucas	35 75	7 14	28 56	7 14	7 14	7 14	Sb, 7 13

Aluminum Bronzes

	Cu	Al	Fe	Zn	Sn	Other Elements
Aluminum Tin Bronze	85 5	2 5		2	10	
Tensilite	64	3 1	1 2	29	0 2	Mn, 2 5

Copper-Manganese Alloys

	Cu	Mn	Fe	Zn	Sn	N1	Other Elements
Manganese Copper	85 55	10 66	2 66		0 39		Pb, 0 45
Manganese Copper	84 33	10 61	2 31	2 1	0 4		Pb, 0 3
Manganese Brass	53 51	3 24	1 44	38 28	1 22	2 14	
Manganese Brass	60 15	2 34	1 19	34 9	0 94		Al, 0 23, Pb, 0 39
Manganese Brass	53 4	1 7	0	39	2 66	2 5	Al, 0 2
Manganese Bronze	82 4	0 6			17		
Manganese Bronze	85 75	0 25			14		
Manganese Bronze	86 3	2 7		5	6		
Manganese Nickel Silver	60	20			10	10	

Tin-Aluminum Alloys

	Al	Cu	Zn	Sn	Mg	N1	Fe	Si	Other Elements
Bourbonnes	48 8	0 25		50 48			0 33		
Fletcher & Emperer Bearing	92 2	7 5		0 25					
Fletcher's Alloy	95 5	3		1 00					Sb, 0 05, PSn 5 added

TABLE 8—*Continued*

	Al	Cu	Zn	Sn	Mg	Ni	Fe	Si	Other Elements
Huron									
Castings A-5	89 90	66		0 5	0 5	1 25			Co, 0 25 and
Ingots									(Mn, Cd, 0 5)
Casting 22	83 7	63	5	5 0					
Krupp (Gros-									
mann) Bearing	87	8		5 0					
Liberty Piston	76 6	1 06	21 3	0 12			0 47		Pb, 0 33
Magnalium									
Cast y	96 0	1 75			1 5				Sn and Pb
Cast z	94 36	0 21		3 15	1 58				Pb, 0 7
Magnalite	92 94	2 59		0 17	1 36	1 70	0 86	0 37	
Manhardts	83 33	6 24		10 00	0 05				P, 0 07

	Al	Cu	Zn	Mn	Sn	Ni	Fe	Si	Other Elements
McAdams, W A	80				8 0				Cd, 8, Ag, 4
McLure	85 4	8 2		0 2	5 0		0 9	0 3	
Mock Silver	84 2	5 5			10 2				P, 0 1
Partinium	96 0	0 64			0 16				Sb, 2 4, W, 0 8
Romanium	97 43	0 25			0 15	1 75			Sb, 0 25, W, 0 1
Rosein	30				20 0	40			Ag, 10
Wolframium	97 17	0 375			1 0				Sb, 1 44, W, 0 0
Zeppelin Alloys									
Channels	88 68	0 7	9 1	0 45	0 15		0 43	0 49	
Angles	90 27	0 73	7 8	0 27	0 11		0 45	0 37	
Zisium	83	1	15		1 0				
Al-Cu-Zn Strong									
Ingot	82 7	3 15	12 8	0 39	0 12		0 48	0 19	Pb, 0 19
Ingot	82 8	5 52	9 9	0 18	0 27		0 81		Pb, 0 3

Tin-Base Alloys

	Sn	Sb	Cu	Pb	Other Elements
Algiers Metal	94 5	0 5	5		
Algiers Metal	90	10			
Algiers Metal	75	25			
Ashberry Metal	82 47	14 43	2 06		Zn, 1
Ashberry Metal	79 80	15 15	3 03		Zn, 2 02
Britannia	77 8	19 4	2 8		
Britannia	77 9	19 4			Zn, 2 8
Argentin	85	14 5	0 5		
Aluminum Solder	85–50				Zn, 15-50
Burgess	76				Zn, 21, Al, 3
Frismuth	69 07			27 83	Al, 3 09
Grimm's	69 1			28 8	Zn, 1 44, Ag, 0 72
Grimm's	50			25	Zn, 25
Wegner & Guhr's	80				Zn, 20
Wilmotts	86				Bi, 14
	87–73				Zn, 8-15, Al, 5-12
	33 36			22 21	Zn, 44 42
Various	47 5			47 5	Ca, 5
	49 5	3 43	1 1	26 06	Zn, 20 31
	85				Al, 10, PSn, 5
Babbitts, Original	89	7 3	3 7		
Babbitts, Hard	83 3	8 3	8 4		
Bearing					
Navy	89	7 3	3 7		
Navy	91	4 5	4 5		

TABLE 8—*Continued*

	Sn	Sb	Cu	Pb	Other Elements
Prussian	91	6	3		
Prussian	90	6	4		
Russian Railroad	90	8	2		
Automobile, American	89	7	4		
Automobile, American	89 3	8 9	1 8		
Automobile, American	88 9	7 4	3 7		
Automobile, American	87	7	6		
Heavy	85	7 5	7 5		
French Car	83 3	11 1	5 5		
German Railroad	83	11	6		
Valve Rods, etc	82	10	8		
French Railroad	82	12	6		
Piston	81	12 5	6 5		
Swiss Railroad	80	10	10		
English	74 47	17 96	7 57		
German	84 44	7 78	7 78		
Prussian	66 66	13 5	9 99	9 54	Zn, 0 16 , Fe, 0 2
Prussian	73	18	9		
Prussian	72	26	2		
(Kamarsch)	71 4	7 2	21 4		
Valve Packing	71	24	5		
German	70 8	15 1	4 9	9 2	
(Kamarsch)	70 7	19 7	9 5		
G W R England	67	11	22		
French Railroad	67	22	11		
English Railroad	90	7	3		
German Ludenscheidt	71 8	24 3	3 85		
Britannia					
English	94	5	1		
English	95 23	3 40	1 36		
English	92 0	6 13	1 84		
English	90	8	2		
English	90	6	2		Bi, 2
English	90	7	3		
English	85 5	9 7	1 8		Zn, 3
Cast	90 6	9 2	0 2		
Cast	85 5	10 5	1		Zn, 3 0
Cast Tutania	91 4		0 7	7 62	Zn, 0 25
Cast Tutania	92 35	4 65	2 45	0 32	
Birmingham I	90 57	9 38	0 03		
Birmingham II	85 5	10 5	1		Zn, 3 0
Sheet	91 5	7 1	1 4		
Sheet	90 6	7 8	1 5		
Spinning	93 7	3 75	2 6		
Spoons	88 4	8 7	2 9		
Spoons	85 5	14 4	0 15		
Spoons	84 7	5 0	3 7		Bi, 4 9 , Zn, 1
Spoons	88 42	8 68	2 8		
Spoons	85 42	14 42	0 15		
Spoons	84 46	5 62	3 68		Zn, 1 53 , Bi, 4 88
Plate, Hard Spelter	90 62	7 81	1 46		
Plate, Birmingham	91 46	7 12	1 4		
Plate, Tutania	90		2 7	6 0	Zn, 1 3
Plate, Deutsch (Luden-scheidt)	71 85	24 26	3 85		
German	84	9	2		Zn, 5
German	81 9	16 3	1 8		

TABLE 8—*Continued*

	Sn	Sb	Cu	Pb	Other Elements
German	70 82	15 10	4 91	9 21	
German, Various, Turn	93 65	3 75	2 63		
German, Queen's Metal	88 52	7 10	3 48		
Blatt-Silver	91 1			0 35	Zn, 8 25, Fe, 0 23
Bushing, Russian	72 2		1 3		Zn, 26 5
Clichier Metal	48	10 5		32 5	Bi, 9
Clichier Metal	80			5	Bi, 15
Deurance Metal (Locomotive)	33 3	44 5	22 2		
Dudley Antifriction	98 13		1 6	0 25	
Fahrig Antifriction	90		10		
Gilding Foil	97 6		2 16		Fe, 0 11
Hard Head	90	8	2		
Hammonia Metal	64 5		3 25		Zn, 32 25
Hoyles Metal	46	12		42	
Husmann Metal	73 6	11	4	10 6	Zn, 0 18, Fe, 0 22
Jacoby Metal	85	10	5		
Kamarsch Bearing	87 99	5 18	3 73		Bi, 1 65, Zn, 1 45
Minofor (Britannia)	68 5	18 2	3 3		Zn, 10
Minofor	66 66	20 2	4 04		Zn, 9 1
Navy Bearing	89	7 3	3 7		
Navy Bearing, Hard	80	15	5		
Parsons White Brass	60		5		Zn, 35
Parsons White Brass	81	11	4 5	3 5	
Parsons White Brass	76	6	5	13	
Pewter	80			20	
Pewter	73 5	5 5	1	20	
Pewter	88 42	7 16	3 54		Zn, 0 88
Pewter	88 86	7 56	1 79	1 79	
Pewter	82 26	5 38	1 51	10 85	
Pewter	89 3	7 6	1 8	1 8	
Pewter	84 7	1 7	6 8		Bi, 6
Phosphor Tin	95				P, 5 0
Phosphor Tin	90				P, 10
Plastic Metal	80 5	8 6	9 5		Fe, 1 4
Poterie D'Etain	90	9	1		
Prince's Metal	84 75	15 25			
Queen's Metal	52 60	17 19		17 19	Zn, 13 02
Queen's Metal	87	8 5	3 5		Zn, 1
Queen's Metal	73 36	8 88		8 8	Zn, 8 88
Queen's Metal	88 5	7 1	3 5		Zn, 0 9
Queen's Metal	88 5	7	3 5		Bi, 1 0
Ships Nail Alloy	50	17		33	
Silver Foil	90				Zn, 10
Silver Foil	97 5		2 5		
Stanniol	96 2		1	2 4	Ni, 0 3, Fe, 0 1
Tinfoil	87 5	0 5	4	8	
Tourun Leonard's Metal	90		10		
Trabuk Metal	87 5	5			Ni, 5 5, Bi, 2
Tinsel	60 4			39 6	
Tutania, Cast	91 4		0 7	7 62	Zn, 0 25
Tutania, Cast	92 4	4 6	2 5	0 32	Fe, 0 13
Tutania, English	80	16	2 7		Zn, 1 3
Tutania, Plate	90		2 7	6 0	Zn, 1 3
White Metal, Hanover	86 8	7 6	5 6		
White Metal, Dutch	81 5	8 8	9 6		

TABLE 8—*Continued*

Lead-Base Alloys

	Pb	Sn	Sb	Cu	Other Elements
Accumulator Metal (Condenser Foil)	90	9 25	0 75		
Aluminum Solder, Frismuth	27 84	69 07			Al, 3 09
Antifriction	77	10	12 5	0 5	
Antifriction	77	8	14	1	
Bearing	80 5	11 6	7 4	0 5	
Bearing (Katzenstein)	76 0	7 15	16 45	0 4	
Bearing	73 0	8 5	18 0	0 4	
Bearing	68 0	9 6	20 5	1 6	
Bearing	71 57	7 76	18 64	2	
Bearing	62 5	26 2	10	1 3	
Bearing	61 0	25 0	13 0	1 0	
Bearing	48	40	10	2	
Bearing (American)	46	36 5	16 5	1 0	
Bearing	40	42	16	2	
Bearing	37	50	12	1	
Bearing	25 5	61	10 5	2 8	
Bearing	11 8	74	9 5	4 7	
Bearing	10	75	12	3	
Bearing	86	1	13		
Bearing	77 2	7 69	7 69	7 41	
Bearing	82	2	16		
Bearing	80	10	10		
Bearing Compagnie de l'Est	80	12	8		
Bearing	80	5	15		
Bearing	76	7	17		
Bearing, American Railroad	73 5	8	18 5		
Bearing, French Railroad	70	20	10		
Bearing, Paris-Lyon-Mediterranean Railroad	70	10	20		
Bearing, American Railroad	68	21	11		
Bearing, Graphite Metal	68	15	17		
Bearing	62 63	27 27	10 1		
Bearing	60	20	20		
Bearing, Chemin de fer de l'est Franc	42	42	16		
Bearing	40	45	15		
Bearing, Italian Railroad	37	38	25		
Bearing	10	75	15		
Capsule Metal	92	8			
Clichier Metal	46	33			Cd, 21
Clichier Metal	50	36			Cd, 14
Clichier Metal	32 5	48	10 5		Bi, 9
Clichier Metal	5	80			Bi, 15
Electrotype Metal	93	3	4		
English Linotype	83	5	12		
English Stereotype	82 5	4 5	13		
Fahlun Brilliants	40	60			
Foil-Lead (Calin)	86 5	12 5		1 0	
French Auto	75	10	15		
For Small Castings	5	75	20		
Ghevor Bearing	76 5	8	14		Fe, 1 5
"Glyco"	80 5	4 5	14 5		As, 0 5
Hard Lead	57 76	33 22	8 66	0 36	
Hoyle's Metal	42	46	12		
Hoyt Metal	96–90	1	3 9		
Jacana Metal	70	10	20		

TABLE 8—*Continued*

	Pb	Sn	Sb	Cu	Other Elements
Locomotive Bushing	73 05	9 8	17 15		
Linotype Metal	85	3	12		
Mackenzie Metal	70	13	17		
"Magnolia"	78	6	16		
"Magnolia"	79 75	5	15		Bi, 0 25
Marine Babbitt	72	21	7		
Metallic Packing	94 54	5 46			
Metallic Packing Compagnie d'Orleans	76	14	10		
Non-Pareil	78 35	4 95	16 7		
Noheet	98 41	0 08	0 11		Na, 1 4
Pewter	10 85	82 17	5 38	1 6	
Pewter	20	80			
Piston Packing, Compagnie de Nord	73	12	15		
Solder	60	39	1		
Plumbers	66 6	33 3			
Half and Half	50	50			
Tinman's	33 3	66 6			
Stereotype Metal	82	6	12		
Stereotype Metal	82	3 2	14 8		
Stereotype Metal	76	4	20		
Stereotype Metal	70	7	23		
Stereotype Metal	65 69	16 66	17 65		
Stereotype Metal	35	60	5		
Tandem	77 39	5 88	16 73		
Tea Lead	98	2			
Terne Metal	81 71	16 67	1 62		
Type Metal	70	10	18	2 0	
English, Old	69 55	9 15	19 59	1 71	
English	63 2	12	24	0 8	
English	60 5	14 5	24 2	0 8	
Krupp	59 6	12	18	4 7	Ni, 4 7 , Bi, 1
English	58	15	26	1	
English	77 5	6 5	16		
German	75	2	23		
German	60	35	5		
German	60	34 6	5 4		
German	60	15	25		
Common	60	10	30		
Common	55 5	40	4 5		
Best	50	25	25		
French	55	22	23		
French	55	15	30		
White	77 54	5 03	15 1	2 3	
White	33	53	10 6	2 4	Zn, 1
White	33 9	49 1	13 6	3 3	

Zinc-Base Alloys

	Zn	Cu	Sn	Sb	Pb	Other Elements
Aluminum Solder, Frismuth	47 26	5 5	31 34			Al, 10 4 , Ag, 5 5
Aluminum Solder, Frismuth	47 4	5 3	36 8			Al, 10 5
Aluminum Solder	30		65			Bi, 5
Aluminum Solder, Cornande and Cruiys	52		30			Al, 17 5 , Ni, 0 5

TABLE 8—*Continued*

	Zn	Cu	Sn	Sb	Pb	Other Elements
Aluminum Solder, Richards	25		71 5			Al, 3 5
Battery Plates	63 4	3 2	21 3		12	
Babbitt Metal	63 89	4 63	24 07	2 78	4 63	
Bearing, Hard	90	7	1 5	1 5		
Bearing	88	8	2	2		
Bearing	85	5	10			
Bearing	77	5 5	17 5			
Bearing, English	75 22	8 22	16 56			
Bearing	66 5	4 2	29 3			
Bearing	55 28	0 55	22 81		1 26	Al, 20 1
Biddery	90 2	6 3	0 8		2 6	
Biddery, Henie's	84 3	11 4	1 4		2 9	
Britannia, Cast	47 52	2 98	47 52	0 99	0 99	
Dunnlevic and Jones	52	1 6	46	0 4		
Ehrhardt's Metal	89	4	4		3	
Ehrhardt's Type	89	3	6		2	
English White Metal	76 74	5 64	17 62		2	
Fenton's Alloy	80	6	14			
Glievor Bearing	73 5	4 4	6 7	9	5	Cd, 1 4
Heavy Axle	48 96	1 04	39 58	6 25	4 17	
Hammonia Metal	32 25	3 25	64 5			
Iridium	77 25	1 12	21 63	Trace		
Iridium	83 00	1 25	15 75	Trace		
Kneiss Metal	50		25		25	
Kneiss Metal	40	3	15		42	
Ledebur's Bearing	77	5 5	17 5			
Parsons White Brass	30	5	65			
Pierrot Metal, Beugnot	78 81	7 85	7 19	3 31	2 84	
Propeller Bushing	69	5	19	7		
Pump Cocks	72	7	21			
Russian, Packing	98 5		0 98		0 32	Fe, 0 16
Russian	26 5	1 3	72 2			
Salge Metal	85 07	3 98	9 85		1 1	
Schomberg-Bearing	59 4	0 38	39 8		0 21	Fe, 0 15
Silver Leaf	8 28		91 36		0 36	
Vaucher's Alloy	75		18	2 5	4 5	

Fusible Metals

	Bi	Sn	Pb	Cd	Other Elements	Temperature of Fusion
Anatomical Alloy	53 5	19	17		Hg, 10 5	60° C
Bismuth Solder	40	20	40			
Bismuth Solder	33 3	33 3	33 3			
Bismuth Solder	27 5	45	27 5			
Bismuth Solder	25	50	25			
D'Arcet	50	25	25			
Eutectic	52 5	15 5	32			96° C
Eutectic	49 5	13 1	27 3	10 1		70-74° C
Eutectic	54	26		20		103° C
Eutectic		50	32	18		145° C
Fusible Tea Spoons	44 5	16 5	30		Hg, 5-10	
Guthrie's	47 38	19 97	19 36	13 29		
Lictenberg	50	20	30			
Lipowitz	50	13 3	26 7	10		
Newton's	50	18 75	31 25			
Onion's	50	20	30,			

TABLF 8—*Continued*

Rose s	50	22	28	
Rose's	35	30	35	
Wood's	50	12 5	25	12 5

Silver Alloys

	Ag	Cu	Zn	Sn	Other Elements
Silver Solders					
Quick	62 5	20 9	10 4	6 2	
Quick	56 9	27 7	11 5	3 8	
Bureau of Standards	40	14	6	40	

Non-Corrosive Alloys

	Sn	Co	Ni	Cu	Fe	Zn	Other Elements
Non-Oxidizable, Lemarquand	9	8	7 0	39		37 0	
Non-Oxidizable Marties'	10		35	17	10	18 0	Cr, 10

Platinum-Tin Alloys

	Pt	Zn	Sn	Cu	As
Platinum-Gold Cooper s Mirror	9 5	3 5	27 5	58 0	1 5

CHAPTER 11

HOT-DIPPED COATINGS

Historical Development of Tin Plate Industry

Little information is available concerning the early history of tin plate, for secrecy appeared to be the only policy by which early inventors might benefit from their discoveries However, it is certain that the art of coating metal, particularly iron, with tin was known as far back as 25 A D , in the time of Pliny The Romans were credited with considerable skill in plating copper and iron vessels by dipping them in baths of molten tin, or by applying tin to the surface of the heated object The tin plate industry is nevertheless supposed to have originated late in the thirteenth century in Bohemia, where, carefully guarded, its development was extremely slow Visiting that country about 1620, an agent for the Duke of Saxony succeeded in ferreting out enough information to establish a like industry in Saxony By 1665 it was in a flourishing state England, with a large production of iron and with the resources of active tin mines in Cornwall and the Scilly Islands, likewise turned her attention to the manufacture of tin plate Through Andrew Yarranton, details of the methods used in Saxony were carried to England, where experiments resulted in opening up the industry about 1670 It gained little in the succeeding half century, meeting many obstacles to hinder its advance, and it was not until Major Hanbury entered the field in 1720 by establishing a works at Pontypool that anything approaching success could be marked

In Hanbury's plant the base metal was of wrought iron, made by treating charcoal pig iron in small rectangular furnaces To form the base plate, pieces of iron thus prepared were twice heated in a blacksmith's forge and hammered as thin as possible Then several sheets of this metal, packed together, were reheated to redness and hammered down to the desired thickness The low temperature and the formation of oxides on each sheet were guards against the possibility of welding the layers together The small finished pieces, separated from each other, were trimmed to size, ready for cleaning

Since acid pickling was then unknown, the base plates were cleaned by immersing them in fermented barley water for several days After

washing, they were dipped into hot grease to drive off all moisture, then set into a bath of molten tin covered with palm oil Upon withdrawal the plates were brushed, redipped into a second and sometimes a third tin bath, and finally returned to the grease pot to remove any excess tin Bran or barley meal was used to absorb the grease Polishing the sheet with sheep fleece completed the process The coating was evenly distributed over the surface of the plate but was decidedly heavy as compared with the present-day product

Since 1720, marked improvements in manufacturing methods have been adopted, resulting not only in a superior product but in a reduction of costs Chief among them is the first sheet-rolling mill which appeared in 1728 to replace the hammering operation It is thought that both Hanbury and John Payne were responsible for its construction Through its use, base sheets were turned out more pliable, of more uniform thickness, and of a greater size than was possible by the earlier hand methods The sheet mill made Wales the foremost producer of tin plate The perfecting of the steam engine in 1770 further increased the efficiency of the rolling mill, substituting steam for water power in its operation About the same time the idea of replacing charcoal with coke in making wrought iron resulted in the production of two grades of tin plate, referred to as "cokes" and "charcoals" The terms in present-day practice designate only finishes rather than the composition of the base metals Other innovations were injected into the industry, such as the use of sulfuric acid as a pickling agent in 1806 instead of the more crude barley water, the adoption in 1829 of the practice of box annealing of base plates in preference to fire-bed annealing, the invention by Morewood about 1863 of a device for carrying the sheets out of the tin bath through a set of rolls located in the oil layer, insuring uniform distribution of the tin During 1874 an attempt was made to manufacture tin plate in the United States Works were erected at Demmler, Pa, by the United States Iron and Tin Plate Company, and at Wellsville, Ohio, by the American Tin Plate Company However, competition from the imported tin plate proved too great, and in 1878 both plants were obliged to divert their efforts to the manufacture of light sheets, largely for enameled ware Attempts made at the Demmler works in 1876 to roll Bessemer steel into sheets, resulted in the general substitution of steel for iron in making tin plate in England Other changes and refinements included the cold rolling of the black base sheet, giving a much improved finish, the use of a flux instead of grease to take out all moisture prior to tinning, the mixing of lead with tin to give a dull finish or terne plate, the in-

vention of power driven trimming shears As a result, Wales continued to lead the world, as far as the tin plate industry was concerned, for more than 175 years It is reported that in 1890 her output of tin plate exceeded 13,000,000 base boxes, of which about 70 per cent was exported to this country In that year, the McKinley tariff bill placed a protective tariff of 2 2 cents per pound on tin plate The following year, when the bill went into effect, the Demmler works resumed tin plate manufacture, and the industry began to grow in various sections of the country Due to government protection and to the invention of automatic can-making machinery, the annual production of tin plate in the United States now exceeds 30,000,000 base boxes

Method of Tinning

The application of the tin coating to steel is only a very small amount of the work involved in the manufacture of tin plate The rolling of the black plate is similar to the manufacture of light sheets The original "tin bar" is of soft steel, known as tin plate quality The greater portion of the steel is produced by the open hearth process, although it is also produced by any of the standard steel-making methods More than two-thirds of the tin plate made requires black plate between 30 and 34 gage (U S S G), that is, between 0 5000 and 0 3437 pound per square foot

The steel plate is prepared for tinning by pickling mechanically in 4 per cent sulfuric acid at 180° to 190° F for 8 to 10 minutes The pickling loss, as the result of scale removal, is about 2 per cent by weight This operation is termed "black pickling" After black pickling, the sheets are annealed in closed boxes sealed with sand This operation, termed "black annealing," is done at 1400° F (760° C), the sheets being brought up to temperature slowly, remaining in the furnaces 16 to 18 hours, and then slowly cooling to room temperature in 40 to 48 hours Annealing removes rolling strains and stresses and adsorbed gases due to pickling, it eliminates brittleness and clears up the surfaces of the plates

After pickling and annealing, the plates are cold rolled to improve the etch-roughened and porous surface resulting from the previous operations Cold rolling also flattens the plates To remove the slight hardening resulting from cold rolling, the sheets are "white"-annealed at 1020° F (550° C), being brought to temperature in 10 to 12 hours, and then allowed to cool slowly to room temperature

Light films of oxide result from the cold rolling and white annealing These are removed by "white" pickling by machines in 2 per cent

sulfuric acid, at lower temperatures than black annealing, for 3 to 5 minutes It is distinctly desired to avoid etching of the plate Over-pickling will cause the plate to take up larger amounts of tin and make it more difficult to obtain bright-polished and lustrous surfaces on the final tin plate The plates are carefully washed in clean cold water and inspected They are stored in water boshes (to which small amounts of hydrochloric acid are added to prevent surface oxidation of the plate) until needed for tinning

A tinning stack consists of a tinning pot for holding the molten tin, a furnace for heating the pot, a tinning machine for mechanically carrying the plate through the tin, a cooling table for receiving the tinned plate and delivering it to the cleaning and polishing machine A tinning set consists of a pot and its setting, the furnace, and the tinning machine Most of these are simple in construction, although some, such as the Thomas, designed to white pickle, wash, tin, clean, and polish the plates automatically, are quite complicated

The simplest form of tinning machine consists of four high carbon steel rolls, held in place in heavy housings, and arranged in two pairs so that the rolls in each pair lie in the same horizontal plane and the gripping faces of the rolls in the two pairs lie in the same vertical plane At one end the rolls of each pair are geared together At the other end one roll in each pair carries a larger gear which meshes with an idler mounted between the two pairs The gear on the top roll is driven by a small motor The rolls are thus revolved in a manner to draw the plates upward when they are inserted between the rolls of the bottom pair

The tinning pots vary in size according to the machine They are made in one piece of close-grained cast iron They consist essentially of two long narrow chambers separated by a partition extending almost to the bottom and by an elevation in the bottom that rises to within 3 or 4 inches of the bottom edge of the partition The opening thus made permits a continuous bath of molten tin in the bottom of the pot, and provides a passageway for the plate to pass from one chamber to the other The first or entering chamber is seldom more than 2 feet deep, while the other or finishing chamber is about 4 feet deep and projects above the first Both chambers are sloped inward from the vertical The pot is mounted in a brickwork furnace setting, so that the tin or entering chamber projects about 9 inches into the combustion chamber Hoods are set over the tinning machine and the pot to take off fumes A modern tinning unit (two stacks) in a large tin plate plant is shown in Figure 84
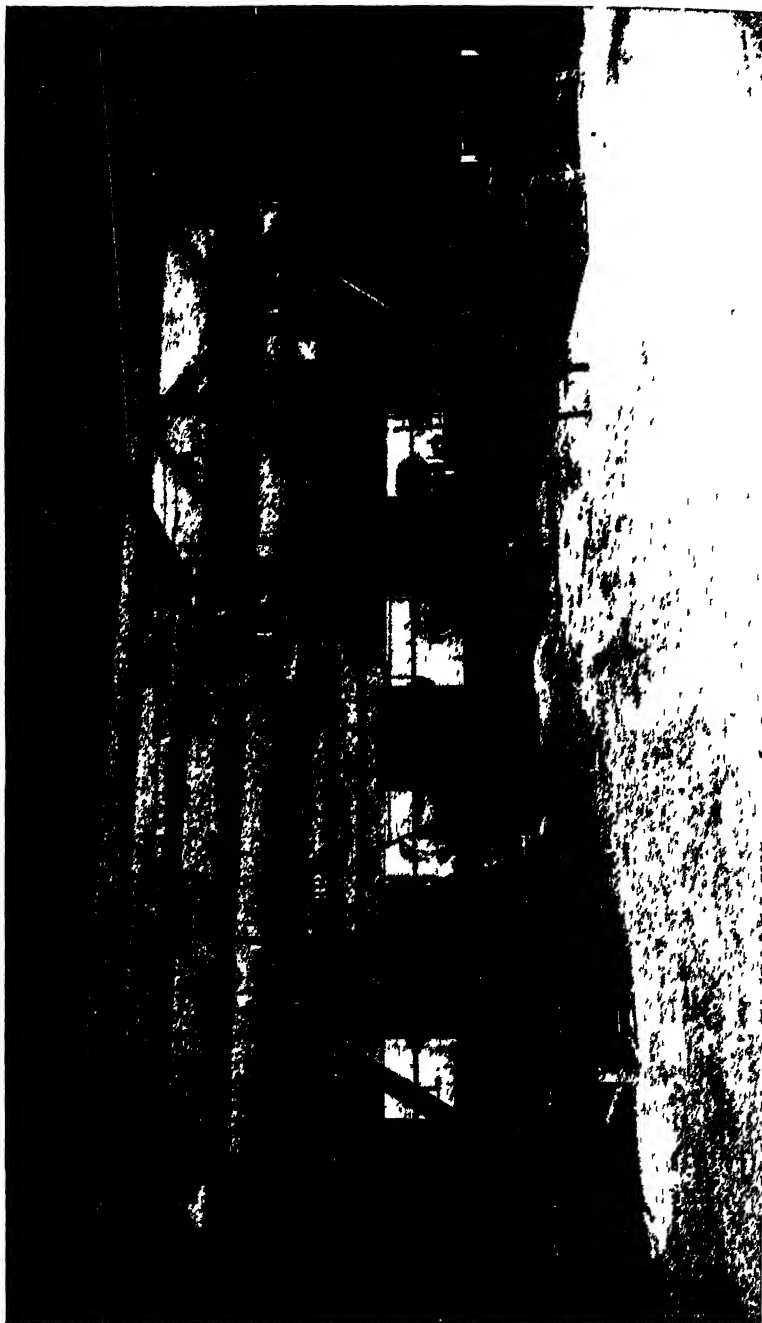
Fig. 84—Commercial tinning plant
(Courtesy American Sheet and Tin Plate Co.)

When operation is begun, the pot is filled with molten tin to within about 3 inches from the top of the entering chamber This brings the surface of the tin about half a foot above the slit or opening in the partition between the chambers, closing the slot except through the tin Pots usually require from 5,000 to 10,000 pounds of pure tin, of Banka or Straits grade or the equivalent The upper part of the exit chamber is now filled with palm oil The tinning machine is immersed in the molten oil and is suspended from the top of the chamber The tin and oil levels are adjusted so that the lower pair of rolls of the machine are about 2 to 3 inches above the tin level, and the exit rolls at the top of the oil layer are partially exposed for ease of inspection On the entering side of the pot, the narrow flux box, of the same length as the rolls, is inserted so that its lower edges dip into the molten tin and its upper edge is elevated above the top of the chamber The flux box holds the fused mixture of zinc and ammonium chloride used to keep the sheets clean and dry and flux them preparatory to tinning

Tinning is performed either by hand or mechanically In both cases the pickled and soaked sheets pass through the flux into the molten tin, through the tin and the slot in the partition between the chambers, then up to the nip of the lower rolls of the tinning machine in the palm oil The rolls draw the tinned sheet through the palm oil and deliver it to raising rolls and frames which drop it on an incline to a conveyor Mechanically fed tinning pots, through increases of speed, have more than doubled the output per pot of hand tinning, and permit the production of brighter and more uniformly coated plates

The thickness of the tin coating is a function of the temperature of the tin and the palm oil, within certain limits, the speed of the plate through the tin, and the tightness of the rolls of the tinning machine Tin in the entering chamber is kept at about 575° F The temperature of the oil in the exit chamber is about 475° F, being heated from the molten tin underneath The temperature of the tin in the second chamber must be considerably cooler than the tin in the first section, otherwise the plate will not be as brilliant and lustrous as is desired The oil protects the tin from oxidizing while it is cooling The flux is kept molten by heat received from the tin underneath

The tin plates carry oil on their surfaces They next pass to a cleaning and polishing machine These are arranged in two sets In the first set the sheet is passed through rolls consisting of compressed disks of canton flannel mounted on a long mandrel As the plate passes through the rolls, a constant stream of finely ground cleaning mixture capable of adsorbing the oil falls on the plate The cleaning mixtures

consist of about 25 per cent of rye and wheat middlings and about 75 per cent of soft and fine bran, sawdust, ground peanut hulls, and finely ground corn cobs After the cleaning mixture has adsorbed as much oil as is commercially possible, it is sold for cattle feed The plate cannot be cleaned until it is cooled well below the melting point of the tin After cleaning, the sheets are polished on polishing rolls and then sorted and inspected

The tinning method as described is not practicable for the production of some grades of heavily coated charcoal plates nor for all charcoal plates weighing over 135 pounds per base box These are made by combination dipping in which the sheets are first tinned in the same manner as described under tinning of coke plates, after which they are dipped by hand in a pot of pure tin kept at a low temperature, then into a bath of palm oil and finally passed through a system of rolls by which the excess tin is wiped off and the remainder evenly distributed

The finished plates are classified into primes, seconds, menders, and waste plate Waste plates are detinned and the base metal sent back to the steel plant as scrap Primes cannot be considered as perfect plates They represent the best grade, however Seconds are plates which will give more or less waste or scrap when applied to the purpose for which they are made Poorly cut plates, or plates with small uncoated spots or defects confined to a small area, cannot be classified as primes, but this does not prevent their utilization Menders are plates that contain some defect in the coating that can be corrected by retinning

The assorted primes and seconds are now counted, collected into packs of 112 plates each, and calculated into base boxes of 31,360 square inches each High grade charcoal plates are best packed with tissue paper separating the surfaces of the plates Plates for export are hermetically sealed in tin plate boxes and then enclosed in wooden boxes

The present-day commercial sizes, weights, coatings, and designations of tin plate are given in Table 9

TABLE 9

SIZES AND WEIGHTS OF TIN PLATE

Gage No	Lb per Sq Ft	Lb per Base Box	Symbol
23	1 1250		
	1 079	235	6X
	1 047	228	6XL
24	1 0000		
	0 987	215	5X
	0 964	210	D2X
	0 955	208	5XL
	0 895	195	4X

TABLE 9—*Continued*

Gage No	Lb per Sq Ft	Lb per Base Box	Symbol
25	0 8750		
	0 863	188	4XL
	0 827	180	DX
	0 804	175	3X
	0 771	168	3XL
26	0 7500		
	0 748	163	
	0 712	155	2X
27	0 6875		
	0 680	148	2XL
	0 657	143	
	0 638	139	DC
28	0 6250		
	0 620	135	IX
	0 588	128	IXL
	0 574	125	
	0 565	123	
29	0 5625		
	0 542	118	
	0 514	112	
	0 505	110	
30	0 5000		
	0 491	107	IC
	0 459	100	ICL
31	0 4375		
	0 436	95	
	0 413	90	
32	0 4062		
	0 390	85	
33	0 3750		
	0 367	80	
34	0 3437	75	
	0 321	70	
35	0 3125		
	0 298	65	
36	0 2812		
	0 276	60	
37	0 2656		
	0 253	55	
38	0 2500		

TERNE PLATE

Terne plate is a sheet steel product made by coating the steel sheet with an alloy of lead and tin It is also known as roofing tin, inasmuch as it was first produced for use as a roofing material For this use it is manufactured in sheets of approximately 20 inches by 28 inches and either IC or 107 pounds per base box, the sheet being 30 gage (U S S G), or IX or 135 pounds per base box and about 28 gage thickness Many other uses for terne plate have been developed in recent years, so that perhaps now more than 40 per cent is consumed in the manufacture of articles other than roofing materials It is em-

ployed in containers such as automobile gasoline tanks, oil cans, and other forms of manufactured containers For some of these purposes it is produced in the form known as long ternes, as large as 40 by 120 inches in area and from 16 to 30 gage thickness The smaller size sheet, 20 by 28 inches, is commonly known as short or small ternes

The steel used for the base metal of terne plate must be very ductile and of uniformly good quality to withstand the severe distortion which the material undergoes in its fabricating operations Open-hearth steel is generally preferred The preparation of the sheets for dipping is the same as tin plate mill practice

Terne coatings vary from 12 per cent tin and 88 per cent lead to 50-50 mixtures, according to the intended use Roofing tin is generally about 25 per cent tin and 75 per cent lead Steel can be coated with lead alone The coatings are always porous An alloying agent is necessary, inasmuch as lead does not alloy with iron It appears that the tin first alloys with the iron and this non-tin alloy acts as a binder between the base metal and the lead-tin alloy coat From this viewpoint, the greater the percentage of tin in the mixture, the better, but from a cost standpoint, the tin content should be kept as low as possible Experience has shown that the lowest economical proportion of tin that can be efficiently employed is not less than 15 per cent

Terne plate coatings are comparatively heavy to insure long life The thickness of the coat is expressed in pounds per base box of 112 plates, 20 by 28 inches in size, or just twice the area of the tin-plate base box Coating weights vary from 8 to 40 pounds per base box, the range being 8, 12, 15, 20, 25, 30, 32, 35, and 40 pounds Even with the heavy coatings, all exposed work should be kept well coated with paint to give full protection against corrosion

There are three general methods of coating small ternes, known as the palm oil, the flux, and the combination process In the palm oil process the sheets are first "boiled" for about 20 minutes in palm oil at a somewhat lower temperature than the terne pot They are then dipped into the molten alloy covered by a layer of oil and allowed to soak in the molten metal for several minutes They are then lifted out of this pot, drained, and dipped singly into another terne metal pot of extra fine quality, and immediately transferred to a grease pot containing oil After removal from the grease pot they are cooled, branned, and cleaned In the flux method, the plates are coated in a tinning machine similar to that used for tin plate, and the original drying of the plate before dipping is done in a neutralized saturated solution of

zinc chloride. The combination process provides for redipping of the plates by a combination of the palm oil and flux methods

After the plates are finished, they are sorted and inspected, and divided into four grades known as primes, menders, strippers, and scrap The primes are first grade, while the menders are plates whose defects can be remedied by rerunning Strippers correspond to tin plate seconds, but inasmuch as all heavily coated terne plates must be primes because their application generally requires full size sheets, strippers are reclaimed by passing them through a flux tinning pot in which some of the coating is removed to form primes of a more lightly coated plate Scrap consists of sheets that cannot be reclaimed They are detinned by melting off the coating in furnaces The base metal is returned to the steel mill as scrap

Terne plate is sent to the market in boxes of 112 sheets, stamped with the base weight, the size, the weight of the coat, the finish, and the kind of steel on the ends of the wooden box Due to the nature of lead in the alloy, terne plates do not have the bright lustrous appearance of tin plate As a result of the crystallization of the alloy on cooling, the surface of heavily coated terne plates shows a ramification of more or less fine lines which divide the surface of the plate into small areas almost uniform in size and shape This marking is known as the mottle It appears on plates carrying 12 pounds of alloy per base box or more The fineness or coarseness of the mottle can be controlled by the rate of cooling It is also affected by the presence of antimony in the terne alloy

TINNING OF WIRE

Comparatively little steel wire is tinned, first, because of the high cost of the tin metal, second, because of the extreme difficulty of entirely avoiding pinholes in the tin coating, and third, tin is electronegative to iron and the destruction of the steel base is accelerated when corrosion begins All copper wire which is to receive an insulating covering of rubber compound must first be tinned to protect the copper from the action of the free sulfur in the insulating materials Were the copper not protected, its electrical properties would be affected Tinning of wire is shown in Figure 85 The wire has to be thoroughly cleaned, usually by some sort of pickling, and fluxed in perhaps saturated zinc-chloride solution or fused salts such as zinc chloride or mixtures of it with ammonium chloride, before entering the bath of molten tin As the wire emerges from the tin bath, it passes through a wipe of wicking, such as asbestos After wiping, it goes to the take-up
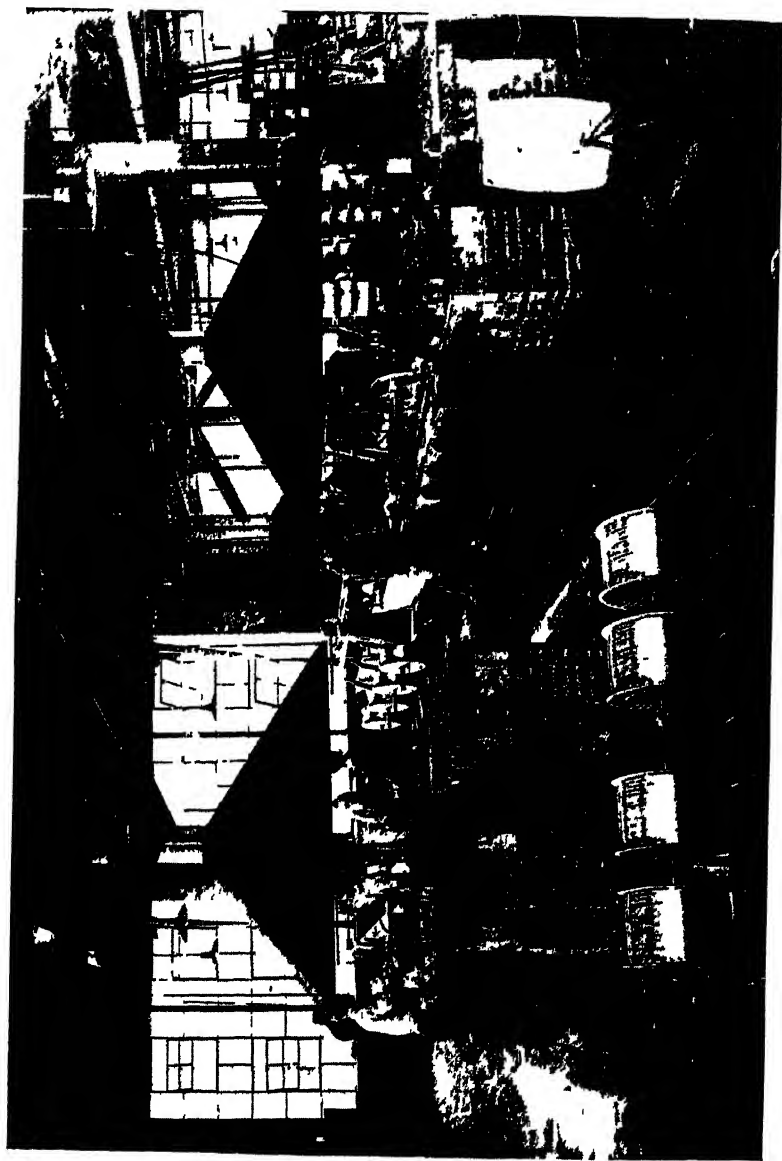
Fig 85—Tinning tanks in a wire-drawing plant
(Courtesy Metal Industry, New York)

blocks, either with or without an intermediate water cooling The temperature of the molten tin during the operation is kept fairly constant at 500° to 550° F If the tin temperature be too low, the coating will be rough, uneven, and more porous, if too high, oxidation will occur with subsequent discoloration due to the formation of yellowish tin oxides .

Pinholes exist in the tin coating on copper wire They form a means of gradual ingress of sulfur vapor from the insulating rubber coating The tin coating is often loosened as a result of the corrosive attack on the copper, sometimes stripping off when the insulation is removed This is usually more evident in the case of old insulated copper wires

TINNING OF COPPER SHEETS

Copper sheets are often tinned by hand operations The tin mixture is melted in a cast-iron pot The copper sheets are cleaned and pickled prior to the tinning process They are then rubbed with a fluxing solution of zinc chloride and hydrochloric acid The operators lay them, one by one, on an inclined table adjacent to the pot A ladle of molten tin is emptied and caused to flow over the sheet, the excess running back by troughs into the pot Then, beginning at the top, the sheet is wiped off with a brush or bundle of tow to remove the excess tin In this manner a smooth, even coating is produced

In another method, the cleaned and pickled sheet is laid on a bench which contains an inset gas grate flush with the top, or else the sheets are heated in a furnace preparatory to tinning In the first method, the sheet is passed over the grate and heated The operator takes small, flat plates of tin of a calculated and weighed amount, lays them on the heated sheet, allows them to melt, and rubs them into the copper sheet when they have melted The flux employed is usually dry, powdered ammonium chloride In the second method, weighed quantities of tin are dropped on the heated sheets as they come from the furnace As the tin melts, it is brushed on to the sheet by means of bundles of tow or brushes as rapidly as possible, and spread over the whole surface of the sheet Manufacturers claim that this method gives a more uniform coating than when molten tin is caused to flow over the sheet

Tinning mixtures containing a small amount of lead are often used, as it is claimed that the latter exerts no harmful effect provided the material is not used in containers for foodstuffs or liquids for drinking purposes, but that the lead has the advantage of increasing the fluidity of the mixture

Tinning of Small Articles

A large number of previously stamped or fabricated articles or parts of sheet metal, mostly steel but often of other non-ferrous materials, are coated with tin by hot dipping This method of tinning seemingly is quite simple, but examination shows that there must be constant attention to the small details incidental to the production of the finished piece The surfaces of articles to be tinned must be carefully cleaned, usually by chemical methods employing alkali cleaners of various natures to remove grease, followed by pickling with acids such as sulfuric or hydrochloric Tinning procedures vary largely in different plants In some plants the pot of molten tin is covered with a flux consisting of either zinc chloride or mixtures of zinc and ammonium chloride, sometimes with small additions of sodium chloride The article to be tinned is passed through the layer of flux and immersed in the molten tin metal, allowed to coat, and then withdrawn, cooled, cleaned, and in some cases polished In another method, the molten tin is kept free from flux, and the article before dipping is passed into a dehydrating solution consisting of approximately a saturated solution of zinc chloride From the dehydrating solution, the object is dipped into molten tin, withdrawn, the excess allowed to drain off, cooled, and cleaned usually in bran or sawdust Tin-pot temperatures vary from about 525° to as high as 600° F , the average practice being about 560° to 575°

Cleaning practice in some plants is quite complicated, involving, perhaps, grease removal in an alkali cleaner either with or without the aid of electric current, pickling in sulfuric acid, washing, etching in ferric sulfate or similar materials, washing again, and pickling finally in hydrochloric acid before tinning

The quality of the finished product will vary with the care given to the cleaning, the technique of tinning, and the purity of the tin metal employed

Hot-dip tinning is employed in the manufacture of milk cans, so-called "tinware," small pieces, the parts of milk separators, pails, and other articles of the same nature

Tinning pots in small plants are usually gas-fired, and often coal- or oil-fired in larger units The pots are provided with draft hoods to take care of fumes from the decomposition of the flux and from the tin metal The coatings produced by hot dipping by the usual hand methods are considerably thicker than those produced on tin plate

Large objects, such as milk cans, are tinned either in pieces, the tinned parts later being assembled by soldering, or in one piece

Tin Cans

The tin-plate industry found a great outlet early in the nineteenth century in the adoption and development of the tin container The first of these articles was made and patented by Peter Durand, an Englishman, about 1810 Dry foodstuffs, as beans, coffee, etc , had up to this time been packed in reed baskets, called "canisters," the word being derived from the Greek name for "reed " Durand's invention accordingly became known as the "tin canister " Increased usage in trade among the early canners shortened the name for convenience to its present form of "can "

In the beginning, tin-can manufacture was a hand process, extremely slow and correspondingly expensive A skilled tinsmith could complete only about 60 cans per day With hand shears and a soldering iron for equipment, he cut the body blanks from the tin plate sheet, shaping them by hand He joined the edges with solder, often ⅛ inch thick A circular piece whose edges were hammered up with a mallet was soldered on to form the bottom The top was a similar disk, in which a small hole had been cut, fixed in place in the same way after the can had been packed The hole served as a vent for the escape of air when the can was heated to preserve its contents A drop of solder closed it while the can was still hot

Since the tin can was developed primarily to preserve food products, the question of lessening the amount of solder in its manufacture became immediately important The present-day tin can is the result of a long succession of improvements in material and fabrication over the first hand-made "canister " One modern type is the sanitary can, used more largely in America than on the Continent This variety has for its distinctive feature the elimination of practically all solder by the use of a gasket of a rubber compound for joining the ends to the body The top diameter is equal to the diameter of the container itself

The manufacture of the modern can involves more apparatus and machinery than does canning itself An automatic slitting machine cuts the tin plate sheets into strips, some narrow to be used in stamping out the ends, others of a width corresponding to the circumference of the can To insure smooth joints, these body blanks are notched at the corners They are then sent to the lock-seaming machine, where the first operation turns back the edges As the sheet is shaped around the mandrel, these edges lock together, flattened by the pressure of a hammer The lock seam thus formed is not always air tight It is therefore run through a bath of molten solder, the excess brushed off, and

the cylinder air-cooled This step in the process of manufacture turns out varying shapes of containers, from the simple cylinder to the odd forms used for cosmetics and similar products

Convex plungers are now forced into the ends of the cylinder, pressing the edges outward and forming flanges upon which to fit the top and bottom Can ends are cut out of the narrow strips of tin plate, produced at the beginning of the process, by means of a press This machine stamps at the rate of about 10,000 to 12,000 disks or tops per hour, working in such a manner as to avoid unnecessary waste of tin Devices to secure rigidity of the ends of the can, such as ridges and depressions, are also formed by the press The edges are turned inward by the next machine in the line The groove thus formed is filled with a rubber compound, perhaps rubber dissolved in benzene, or by a paper gasket, to make an air-tight seam If a solution is used, the can end is quickly dried by heat The double seamer completes the manufacturer's operations by joining one end, called the manufacturer's end, to the body of the can This is done automatically with the can in a horizontal position, small rollers folding the flanges of the end and can body and tightly compressing them Cans are then tested for leaks by subjecting them to compressed air at a pressure of approximately 10 pounds per square inch Leaky cans are retested by hand corrected, and again submitted to the compressor

CHAPTER 12

FOIL AND COLLAPSIBLE TUBES

USES FOR TIN FOIL

Tin can be rolled into very thin plates or sheets The metal is then called "tin foil" or at times "silver leaf" It is stated that a pound of tin may be rolled to an area of 11,000 to 14,000 square inches The usual thickness of foil is from 3½ to 8 mils (0 0035 to 0 0080 in) It is estimated that 5 to 9 per cent of the total tin consumption of the United States goes into tin foil and collapsible tubes

Foils are used to protect perishables against deteriorating conditions They are also used for beautifying and adding to the attractiveness of packages Another use for foil is to be found in the making of electrical condensers Light gage metals are also employed in the manufacture of novelties, such as bon-bon cups, Christmas tree ornaments, tea balls, etc

The metallic covering offered by foils gives a most economical and efficient protection against climatic conditions when they are used for foodstuffs, tobacco, soaps, and similar products An ordinary piece of chocolate, for instance, if exposed to atmospheric conditions without any covering, will become unfit as an edible in a few days If it is wrapped in a foil, it retains its freshness and blend for a period of many months When used in wrapping tobaccos, the metallic covering keeps the moisture content unchanged by preventing evaporation losses Merchandise which has a delicate aroma can well be wrapped in foil, for it prevents the loss of delicate odors such as may be found in the better grades of soap and candies

Foils can be printed and colored, making attractive wrappers Beautiful effects can be obtained by combinations of these colors Since most products today which are sold over the counter are in keen competition with each other, a package which appeals to the eye will unquestionably have a better sale than one which does not In the case of confections where most of the sale value lies in the appearance of the package, it is extremely difficult for a candy wrapped in paper or unwrapped to compete with a good looking, foil-wrapped bar

The ease with which foil can be formed makes it an economical material for forming novelties of various sorts

Tin is soft enough to be cut with a knife, but it files very badly as it chokes up the teeth of a file, except when such a file has been plated with chromium metal It is softer than gold but harder than lead The relative hardnesses on the Von Moh scale are lead 1 5, tin 1 8, and gold 2 5 The variation of the Brinell hardness of tin with temperature is shown in Figure 86 Tin is slightly work haidened, as for example by hammering or rolling, but it anneals spontaneously at ordinary temperatures Tin is most ductile at a temperature in the
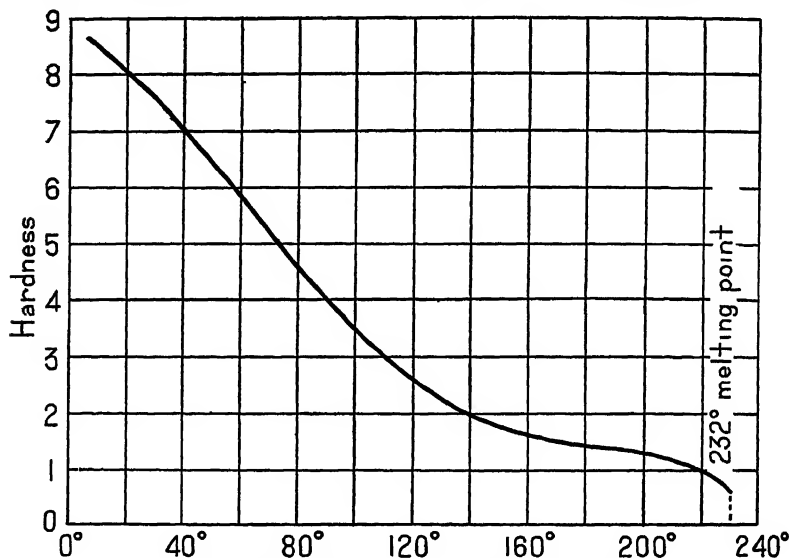
Fig 86 —Hardness of tin at different temperatures

vicinity of 100° C , at about 200° C it becomes so brittle that it breaks to pieces when hammered At that temperature the metal can be pulverized in a mortar

The pressure required to produce plastic flow of tin through an aperture increases regularly with temperature No discontinuity corresponding with the transformation of tetragonal into rhombic tin is observed The plastic flow of tin depends on its previous history Slowly cooled metal flows under a pressure about one-third as great as that required to cause rapidly cooled cast tin to flow Burton and Marshall [1] found that when the pressure on tin is suddenly increased to 300 atmospheres, the temperature rises 0 277° C When the pressure is released, the temperature falls 0 264° C

[1] *Proc Roy Soc (London)*, **50** 130 (1891)

THE MANUFACTURE OF FOIL

Tin suitable for use in foil manufacture should be very pure, particularly the arsenic content should be the minimum possible Antimony in tin is in solid solution It has been experimentally proved a number of times that the antimony cannot in any way contaminate the foodstuff or sweetmeat for which it constitutes a seal or wrapper

The manufacture of foil itself may be subdivided into a number of stages The tin is first cast into rolling ingots with as smooth a surface as possible The cast slabs are then rolled in a break-down mill The usual type is shown in Figure 87 These mills are of very heavy construction with very large reduction gearing, somewhat along the
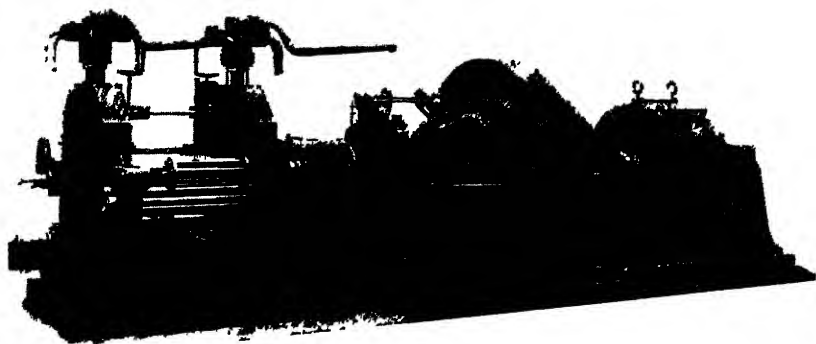
FIG 87 —A break-down mill
(Courtesy Birmingham Iron Foundry)

same lines as steel-mill rolls The metal slabs are rolled in several passes to a given thickness, so that they are thin enough to be sent to the finishing mills These are of somewhat lighter construction, as the reduction in thickness per pass is considerably smaller Such a mill is illustrated in Figure 88 Here the metal slabs are run through a sufficient number of passes to give the required thickness When thin enough, the foil is wound on reels or spools and from there on handled the same as paper Polishing may be done in the finishing mill, the steel rolls of which are very hard, having a scleroscope reading of about 100, ground and buffed to a perfect mirror finish From the finishing mills the foil goes to slitting machines of the conventional type and the product is handled the same as paper. These machines cut the material into the required widths and the product goes to the market in wound rolls

When it is considered that pure tin foils are commonly required six to seven thousandths of a millimeter in thickness, it is easily appreciated, especially by those experienced in the rolling of metals, that satisfactory results can be obtained only by constant attention to metallurgical and other manufacturing details
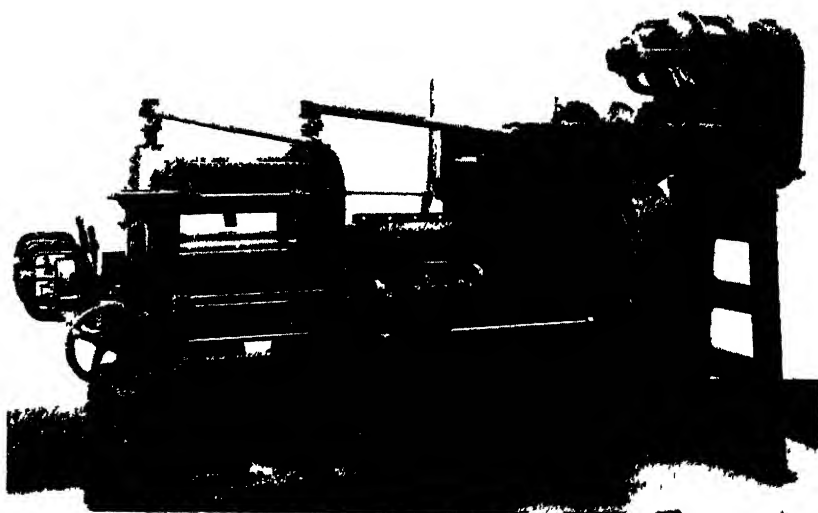
Fig 88 —Finishing mill
(Courtesy Birmingham Iron Foundry)

There is an increasing demand for all the highly decorative lines of tin foil Practically any variation of coloring, embossing, stamping, and printing is now possible The most effective results are obtained with brilliantly colored lacquers On certain colored backgrounds, bronze printing can be applied to produce most attractive results

"Gage" in the trade refers not to the thickness of the foil but to its covering power If one excludes gold leaf, tin foil ranks among the thinnest of metal sheets

COMPETITIVE FOILS

There are four principal kinds of foil These are pure tin foil, foils made from an alloy of lead and tin consisting of about 85 per cent tin, 15 per cent lead, and the two competitors of tin foil—lead foil and pure aluminum foil In addition there is sometimes made a tin-lead foil produced from the rolling of lead and tin sheets together to give

a tin surface to a lead sheet Alloy foils of tin and lead range from comparatively thick tin-coated lead, having about 1 per cent of tin in the core and ½ to ¾ per cent tin on each face, up to a 95 per cent tin-5 per cent lead alloy

In the preparation of these foils, the chief defect met with is minute perforations in the finished sheet With exceedingly thin material, immunity from pinholes is not easily obtained

Inasmuch as different thicknesses of each of the above metals may be employed for certain purposes, there is not much to choose from, considered from a competitive standpoint, when the protective properties are considered In recent years aluminum, at least in the United States, has been a very serious competitor of tin foil, almost entirely displacing it in the field of chocolate wrapping because it holds chocolate products better than any other grade of approximately the same thickness Chocolate blends have a tendency to separate out the cocoabutter when exposed to mildly warm temperature and sunlight Aluminum foil, by actual test, prevents this occurrence more than any other When foodstuffs are being considered, however, it is to be noted that foils containing lead are poisonous While in the United States they may be used for wrapping edibles if backed with paper, many countries have passed food laws which prohibit the use of any wrapping containing lead even when paper mounted This cuts down the kinds of foil which may be used for this purpose to pure tin and aluminum

Tin foil has the disadvantage that it has a tendency to darken under certain atmospheric conditions It loses some of its luster Aluminum does not tarnish but keeps its original appearance longer

Aluminum may be had in different tempers It hardens when worked Because of this property, a soft metal may be used and readily formed It will have a desirable rigidity after fabrication

It is well known that tin foil cannot be readily produced in different hardnesses, as the metal does not work harden Aluminum foil may be substituted, having in a number of cases very definite advantages Aluminum is about one-third as heavy as tin It can be readily seen that an equivalent weight of aluminum will have three times the area of tin metal when it is rolled into fine sheet Considered from the market prices of the metals, aluminum foil has an economic advantage per unit of area Fabrication of aluminum foil is more difficult and more costly than the preparation of tin foil

In making electrical condensers, since the area of surface is the only factor which determines the capacity of such a condenser, there is

little choice between the common foils when this factor alone is considered Aluminum has better electrical conductivity It has the disadvantage, however, that it cannot be readily soldered Connections must therefore be mechanical, although spot welding may be employed

In stereotyping and electrotyping, tin foil is used in sheets of considerable area in operations in which impressions are made in a manner similar to the way the school boy obtains impressions of coins in tin foil or silver paper Great care is demanded in this work from the operators Mundy [2] states that "A very unusual and extraordinary use for tin foil is its introduction into big guns, or ordnance, before firing, a very small quantity being added with the charge It is stated that it does much to prevent or diminish the deposit of copper on the rifled bore of the gun, derived from the copper driving band, the thinness of the tin foil presenting the metal in the required state of fine division, and thus facilitating the interaction of the metals with the necessary rapidity "

COLLAPSIBLE TUBES

Analogous to tin foil, there are four principal types of collapsible tubes, those made from pure tin, tin and lead alloys including those made from tin-coated lead, and the competitors made from lead and aluminum

Pure tin tubes are prepared from the purest metal obtainable, usually Straits, Banka, or Billiton, to which is added a fractional percentage of antimony or other suitable hardening constituent

The manufacture of tubes is a stamping, deep-drawing or extrusion operation The most interesting feature is the fundamental operation of extending the body, shoulder, and nozzle of the tube in one pressing operation from a disk of varying size and shape, depending upon the size of the tube to be made The length of engagement between the ram and the die is quite small The tube is squirted out of the space between the two at a rate of flow which the eye can just about follow Caps are stamped or pressed out of the small portions of metal resulting when the sheet has had circular disks stamped out of it Threading of the top of the tube and tapping of the disk are screw-machine operations The caps are of all varieties, from a simple plain type with a sunk milled edge to the regal crown cap The relatively plastic nature of tin permits its being readily formed into exceedingly complicated and decorative shapes

The greater share of collapsible tubes are highly decorated, being

[2] A H Mundy, "Tin and the Tin Industry," London, Isaac Pitman & Sons, Ltd

enameled, printed, lacquered, or embossed by the usual well-known methods Quite often fancy designs are printed on a white or colored enameled background Electric heating for enameling is employed in the most up-to-date plants

Lead tubes obviously have very limited uses because of the poisonous character of lead and its salts Practically the same restrictions apply to lead tubes as apply to lead foil

In recent years the advent of aluminum collapsible tubes has had a very marked effect on the collapsible tin-tube business The tin-tube business is very highly competitive and the margin of profit in the fabrication of these is very small

Aluminum collapsible tubes become an active competitor of tin collapsible tubes in all cases where the product to be packed is non-alkaline or is without chemical reaction when in contact with aluminum It is estimated that 50 per cent of the products formerly packed in tin can be safely packed in aluminum, and an additional 25 per cent of the total is susceptible to a treatment whereby a slight change in formula will prevent reaction with aluminum

It is difficult to make a comparison of the prices of tin and aluminum tubes, but it seems fair to state on the basis of present tin and aluminum base prices that aluminum can be profitably sold at a price ranging from 10 to 50 per cent lower than tin, depending upon the size Obviously the maximum saving is found in the larger tubes where the metal saving is greater

The base price of aluminum today is less than one-half the base price of tin per pound, with the additional advantage that aluminum is only one-third as heavy as tin This means that, other conditions being equal, a unit of aluminum at present prices will go six times as far as the equivalent of tin, dollar for dollar. Aluminum is not as readily fabricated as tin, and a good part of the saving in metal cost is absorbed by increased labor and tool costs Aluminum-tube extrusion requires better tools and heavier press equipment than tin The cleaning and annealing operations required for aluminum-tube manufacture are not necessary for tin

The thickness of metal used in tube manufacture is practically the same for both metals It ranges from a minimum of 0 0035 to a maximum of 0 008 inch

CHAPTER 13

TIN COMPOUNDS

، Chemically tin is related to silicon, titanium, zirconium, germanium, and cerium The metal is not chemically affected by hydrogen It is stated that it is possible to make tin hydrides The yields are exceedingly small, being less than a few thousandths per cent The formula is stated to be SnH_4, the compound having a melting point of $-150°$ C and a latent heat of 4 55 Cals The gas decomposes spontaneously in a few days when kept in glass vessels at 100m temperatures, and instantaneously above 145° C It is unstable in contact with desiccating agents such as calcium chloride and phosphoric oxides Paneth and Rabinovitsch [1] state that it is unaffected by dilute solutions of alkali hydroxides, of sulfuric and nitric acids, and of most metallic salts, but it is completely adsorbed by solid alkali hydroxide, soda lime, and solutions of silver nitrate or sulfate, which salts are reduced

STANNOUS OXIDE

Very little accurate data in reference to stannous oxide exist in the literature Stannous oxide is a blue-black, iridescent, crystalline substance It is reduced by some reducing agents On the other hand, even mild oxidizing agents readily oxidize it to stannic oxide or metastannic acid It is easily soluble in non-oxidizing mineral acids and in a number of organic acids to form the corresponding stannous salt

Various experimenters have failed in attempting to get pure stannous oxide, using stannous chloride as a source, treating with soda, forming the hydroxide, heating the same, filtering, and washing Sufficient oxidation or hydration took place during these procedures so that a heavy precipitate of stannic oxide was formed

Ditte [2] gives the following rapid method which he claims is perfectly satisfactory for the preparation of pure stannous oxide Stannous chloride is dissolved in water and treated while hot with the smallest amount of concentrated hydrochloric acid necessary to clear the solution The stannous hydroxide is then precipitated by the addition of a soda solution (e g , a carbonate) which is added in small amounts

[1] *Ber*, 57B 1877 (1924)
[2] *Pogg Ann*, 27 145 (1882)

until the mixture is just alkaline to phenolphthalein but not to litmus, which is too alkaline The milk-white solution is then kept at 110° C for several hours After two to three hours the white material changes to a blue-black substance, stannous oxide, with its characteristic metallic sheen The material is then washed by decantation, dried, and made ready for use

Fraenkel and Snipischsky[3] repeated Ditte's method successfully Numerous methods are proposed in the literature for SnO preparation but practically all of them, except Ditte's, produce contaminated products

Following the method of Ditte, stannous oxide was prepared from pure stannous-chloride crystals The strict adherence to his directions as to control of alkalinity is the most important factor in the production of pure SnO Solutions too highly alkaline (greater than pH 7) cannot be made to yield stannous oxide even after several hours boiling Within the range of pH 5 to about pH 6 5, stannous oxide can be readily produced The product, after filtration, careful washing with distilled water to free the precipitates from chlorides, and careful drying at 110° C, is blue-black, lustrous, somewhat iridescent, and decidedly crystalline The material corresponded exactly to SnO as shown by chemical analysis for Sn by iodine titration

SnO, boiled in distilled water for half an hour, did not produce any stannous hydroxide or metastannic acid which could be determined by visual examination It did not change in color, appearance, or crystalline form, in any manner observable under the microscope

It would, therefore, seem that the reaction

$$Sn(OH)_2 = SnO + H_2O$$

is not readily reversible The thermal data

$$Sn(OH)_2 = SnO + H_2O - 1910 \text{ calories}$$
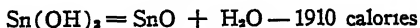
show it to be endothermic

The physico-chemical properties of stannous oxide are important as they are the key of the explanation of the manner in which stannic oxide was reduced by a reducing gas[4] The reduction of stannic oxide may be assumed to take place in either of two ways The stannic oxide may either be reduced directly to tin metal or it may be first reduced to stannous oxide (SnO) which may be further reduced to tin metal

Fink and Mantell[5] have shown that

[3] *Z anorg Chem*, 125 235 (1922)
[4] Fink and Mantell, *Trans Am Electrochem Soc*, 51 175 (1927)
[5] *J Phys Chem*, 32 103-112 (1928)

Stannous oxide is thermally unstable above 385° C, giving Sn and SnO$_2$

Stannous oxide is readily oxidized by both moist and dry air above 240° C At higher temperatures it is pyrophoric

Stannous oxide is oxidized by sulfur dioxide in acid solutions, and reduced by the same reagent in alkaline solution

The reduction of stannic oxide, reasoning from the data on stannous oxide, is a single step reaction above 385° C and a two step reaction below that temperature

TABLE 10

PHYSICAL PROPERTIES OF STANNOUS OXIDE

Electrical conductivity	150×10^{-6} mho	Friederich [1]
Heat of formation	66 8 Cals	Mixter [2]
Magnetic susceptibility	$-0\ 158 \times 10^{-6}$ units per gram,	S Meyer [3]
	$-0\ 012 \times 10^{-6}$ units per mol	" "
Specific gravity	6 9	International Critical Tables

[1] *Z Physik* **31** 813 (1925)
[2] *Am J Sci*, (4) **27** 229 (1909)
[3] *Wied Ann* **69** 236 (1899)

Stannous hydroxide is obtained as a white mass by the addition of an excess of an alkali or an alkali carbonate to an aqueous solution of stannous salts The precipitate is gelatinous and slimy It filters badly It may be washed by suction filtration or decantation The amount of contained water depends upon the method and speed of drying Britton [6] states that stannous hydroxide begins to be precipitated by alkali hydroxide from stannous salts at a pH of 1 9 Freshly prepared stannous hydroxide is white It gradually absorbs oxygen from the air, being converted to hydrated stannic oxide It is only very slightly soluble in water, but readily soluble in acids to form stannous salts Nitric acid oxidizes the material to either an insoluble basic stannic nitrate, metastannic acid, or stannic oxide When stannous hydroxide is treated with solutions of alkali hydroxides, soluble stannites are formed Aqueous ammonia and alkali carbonates do not cause this reaction, however When a little potassium hydroxide is added to a stannous-hydroxide suspension in water at ordinary temperatures, crystals of stannous hydroxide are formed These increase in size until all the hydroxide has been transformed The reaction is cyclic in that at first potassium stannite is formed, this being hydrolyzed by water into stannous oxide, which is less soluble in the solution, and potassium hydroxide, which is thus regenerated to begin the reaction anew Sodium hydroxide acts in a similar way, but ammonia does not Proust [7] states that when stannous hydroxide is mixed with water and cupric carbonate, stannic oxide and crystals of copper are formed,

[6] *J Chem Soc*, **127** 2110 (1925)
[7] *J Phys*, **51** 173 (1800), **61** 338 (1804), *Ann chim phys* (1) **28** 213 (1798), *Nicholson's J* (1) **2** 515 (1798), (2) **14** 38 (1806)

while carbon dioxide is given off Reichard[8] states that stannous hydroxide reduces a solution of arsenic oxide in sodium hydroxide to metallic arsenic The work of Dhar[9] shows that the oxidation of stannous salts is hindered by the presence of easily oxidized organic substances Stannous hydroxide is amphoteric and can function as either a weak base or a weak acid The stannites react with sodium thiosulfate with the formation of stannous sulfide, sodium stannate, sulfite, and sulfostannate On treatment with sulfur, the stannites form stannous sulfide which unites with the excess alkali stannite to form sulfostannites in which the sulfur replaces the oxygen

The stannites are known only in solution They are readily oxidized and chemically act as reducing agents With Fehling's solution, copper oxide is precipitated Alkaline solutions of antimony oxide are reduced to metallic antimony Lead is precipitated from lead salts, and bismuth and lower oxides of the metal from solutions of bismuth salts Alkali stannites do not reduce nitrites and nitrates The stannites are relatively unstable, decomposing into tin and stannous oxide, or they are oxidized by the oxygen of the air to stannates and metastannic acid

STANNIC OXIDE

The properties of native stannic oxide have been discussed under tin ores, ore dressing, and smelting and metallurgy It is very decidedly insoluble in practically all known materials (see leaching of tin ores)

When tin is heated nearly to its boiling point in air, it burns with a white luminous flame The stannic oxide so formed is in a very fine state of subdivision It was formerly known as *Flores jovis* (flowers of Jove) or *Flores stannic* (flowers of tin) When the metal is fused in the air, the surface soon becomes covered with an oxide dross known as "tin ash " This is a mixture of finely divided metal and oxide which can be converted by prolonged roasting to white stannic oxide The product obtained by high temperature oxidation is less soluble in fused silicates It is preferred as an opacifying agent in glazes and enamels Stannic oxide is obtained by treating tin with nitric acid, by oxidizing stannous oxide or stannous hydroxide, by roasting sulfides, or by the hydrolysis of stannic salts or the drying and igniting of stannic hydroxide When a solution of a stannic salt is treated with ammonia, a gelatinous precipitate very difficult to wash is obtained, but if the mixture be warmed with a concentrated solution of sodium sulfate, the dense precipitate is easily washed, and it furnishes stannic oxide upon ignition.

[8] *Ber*, 30 1915 (1897)
[9] *Z anorg Chem.*, 144 289 (1925)

Chemically prepared stannic oxide is usually white or greyish white It differs markedly in many of its chemical properties from native stannic oxide Both forms are readily reduced at temperatures as low as 250° C by hydrogen, carbon monoxide, and similar reducing gases It can be cathodically reduced by electrolytic means It is not affected by air, oxygen, or water Gibbs [10] found fused potassium acid fluoride dissolves stannic oxide When stannic oxide and sulfur are heated together, stannic sulfide is formed Rose [11] states that a molten mixture of sulfur and sodium carbonate transforms stannic oxide into sodium thiostannate He further states that when a mixture of concentrated sulfuric acid is heated with stannic oxide, a syrupy liquid is formed from which all the stannic oxide precipitates upon dilution Molten potassium acid sulfate dissolves stannic oxide When the cold mass is treated with water, the oxide is reprecipitated

Below 500° C the oxide is not affected by nitrous oxide, nitric oxide, or nitrogen peroxide [12] Stannic oxide is reduced to metal when heated with carbon (see Smelting) Moissan [13] states that stannic oxide is reduced to metal when heated with calcium carbide

Stannic oxide is quickly reduced by molten potassium cyanide This was the method employed in the old Cornish assay Milbauer [14] found that molten potassium thiocyanate, when used with stannic oxide, forms stannous sulfide and then potassium thiostannate Carbon tetrachloride reacts with stannic oxide at red heat to form stannic chloride

Stannic oxide is insoluble in fused boric oxide, as shown by the work of Burgess and Holt [15] Lomax [16] showed that the solubility of stannic oxide in fused silicates increases with the proportion of contained alkali

The oxide is reduced to metal by potassium and sodium, magnesium and aluminum

STANNIC ACIDS

Tin and its compounds are amphoteric When tin is precipitated from its salts by alkalies, the resulting hydroxide is soluble in further quantities of the alkali to form salts such as the stannites or stannates In other words, in its simplest forms stannous hydroxide may act as such with a formula of $Sn(OH)_2$ when acted upon by non-oxidizing acids to form tin salts, but when acted upon by alkalies such as NaOH,

[10] *Am J Sci* (2), 37 355 (1864)
[11] *Liebig's Ann* 91 104 (1853), 112 163 (1861)
[12] Sabatier and Senderens *Compt rend*, 120 619 (1895)
[13] *Compt rend*, 125 839 (1898)
[14] *Z anorg Chem*, 42 337 (1904)
[15] *Proc Chem Soc* 19 221 (1903), *Trans Cer Soc* 5 163 (1906)
[16] *Trans Cer Soc*, 11 118 (1912)

TABLE 11

PHYSICAL PROPERTIES OF STANNIC OXIDE

Compressibility coefficient	$3 38 \times 10^{-13}$ Dynes per Sq Cm	Madelung and Fuchs[1]
Dissociation pressure of the oxygen at 927° C ...	$4 47 \times 10^{-15}$	Maeda[2]
Electrical resistance		
On a rising temperature °C	Ohms per Cu In	
360	3550	Doelter[3]
500	1060	"
700	1050	"
900	29	"
1060	5 0	"
1200	1 2	"
1430	0 85	"
On a falling temperature		
1270	0 980	"
1200	1 105	"
1080	1 488	"
1010	1 6888	"
930	2 677	"
780	55 80	"
Hardness (von Moh)	6–7	
Heat of fusion	1 66	Frankel and Snipischsky[4]
Heat of formation		
Sn_{liquid}, O_2 at 800° C	130 26 Cals	Maeda[2]
From solid tin	135 8 Cals	Frankel and Snipischsky[4]
From molten tin	137 46 Cals	Frankel and Snipischsky[4]
Crystalline oxide	137 8 Cals	Mixter[5]
Magnetic susceptibility		
Per gram	$-0 082 \times 10^{-6}$	S Meyer[6]
Per mol	$-0 006 \times 10^{-6}$	" "
Melting point	1132° C	
Specific gravity		
Chemically prepared	6 6–6 9	
Natural crystals	6 7–6 85	
	7 0	International Critical Tables
Specific heat		
0° to 100° C	0 0931	Neumann[7]
Thermal conductivity		
In direction of chief axis	1	Jannettaz[8]
In vertical direction	0 79	"
Thermal expansion coefficient		
16° to 46° C	$a = 0 000004$	Kopp[9]
Cubical, 0° to 100° C	0 0000172	Playfair and Joule[10]

[1] *Ann Physik* (4), 65 289 (1921)
[2] *Bull Japan Inst Phys Chem Research*, 2 350 (1923)
[3] *Sitsber Akad Wien*, 119 70 (1910), *Z anorg Chem*, 67·392 (1910)
[4] *Z anorg Chem*, 125 235 (1922)
[5] *J Am Sci* (4), 27 231 (1909).
[6] *Wied Ann*, 69 236 (1899)
[7] *Pogg Ann*, 23 1 (1831)
[8] *Compt rend*, 75 1501 (1872), *Bull soc min* 15 138 (1892)
[9] *Liebig's Ann Suppl* 3 1 (1864), *Liebig's Ann*, 81 1 (1852), *Pogg Ann* 86 156 (1852)
[10] *J Chem Soc*, 1 121 (1849)

it functions as an acid, H_2SnO_2, to form corresponding salts, the stannites as Na_2SnO_2 In the same way, the following representations of reactions may occur

$$SnCl_4 + 4NaOH = Sn(OH)_4 + 4NaCl$$
$$Sn(OH)_4 + 4HCl = SnCl_4 + 4H_2O$$
$$H_4SnO_4 + 4NaOH = Na_4SnO_4 + 4H\ O$$
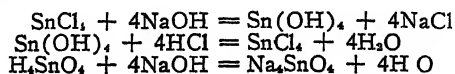
The reactions are not as simple as represented, inasmuch as hydration and hydrolysis occur with the formation of a number of intermediate hydrated substances of varying hydroxyl and water content

When dilute nitric acid acts on tin, depending upon the concentration of the acid, either stannous or stannic nitrate is formed These salts readily decompose with the separation of stannic acid When concentrated nitric acid acts on tin, a white insoluble powder, so-called metastannic acid, is formed with the evolution of considerable heat

Berzelius, in 1811, showed that the compound prepared by the action of nitric acid on tin and the hydroxide precipitated from tin chloride by alkalies, like ammonia, had different properties Both compounds contain the same proportion of oxygen, but possess different characteristics The hydroxide precipitated from stannic chloride is SnO_2 nH_2O, which saturates three times as much base as the hydroxide obtained by the action of nitric acid on tin He likened the former to ordinary phosphoric and the latter to metaphosphoric acid, Fremy designated the former stannic and the latter metastannic acid, while Berzelius designated them α and β stannic acids respectively The α acid is the more basic one It furnishes salts which are readily soluble in water without decomposition The moist material is easily soluble in nitric acid It is also soluble in dilute sulfuric acid to form sulfates, and is easily dissolved in hydrochloric acid to form chlorides The solutions do not gelatinize when they are boiled The β or metastannic acid furnishes salts which are only sparingly soluble in water and are readily hydrolyzed into insoluble basic salts and acids Metastannic acid is insoluble in nitric and even in concentrated sulfuric acid When treated with hydrochloric acid, it unites to form a substance insoluble in an excess of the acid, but soluble in water When the solution is boiled, it gelatinizes

The causes for these differences have not been clearly shown The forms readily change, one to the other One explanatory hypothesis assumes that the acids are colloidal, and that the differences in behavior are due to differences of particle size, another assumes that the acids are isomeric or polymeric forms L Vignon [17] inferred, from his work

[17] *Compt rend*, 108 1049 (1889), 109 372 (1889)

on heats of neutralization of the various stannic acids, that a whole series of variously hydrated compounds exists between the completely water-soluble substance and ignited stannic oxide R Lorenz [18] compared the dehydration rates of the α and β acids and stated that their composition was identical, both existing in all stages of hydration between H_4SnO_4 and H_8SnO_3 The characteristic properties of the compounds are retained after repeated precipitation, but the salts are different Kleinschmidt [19] states that the α and β acids are colloidal substances capable of reversible transformation, and that the change of α to β occurs more readily than β to α Experimental indication of the formation of definite hydrates is seen from the results of a number of workers When gels are prepared from stannic chloride by the action of ammonia and ammonium chloride, at low hydroxyl-ion concentration and in a short time, and the precipitate is dried by acetone at $-35°$ to $-10°$ C, they have the composition $Sn(OH)_4$ H_2O Under similar treatments at room temperature, the composition of the precipitate is $Sn(OH)_4$, or orthostannic acid Stannic acid is transformed in aqueous solutions into more feebly basic acids of the α stannic-acid series Union of several molecules of stannic hydroxide, with loss of water, appears to give a series of polyorthostannic acids with diminishing basic properties

Mecklenburgh,[20] Zsigmondy,[21] and Weiser [22] believe that the differences in behavior of the different stannic acids are due to differences in the sizes of particles β stannic acid is supposed to consist of the largest primary particles Franz [23] assumes that the primary particles are less than a micron in size, and that there is a gradual grouping of molecules, through formation of complexes, to larger secondary particles The particular properties, therefore, of any stannic acid may be considered to be a function of the grain size, which in turn is dependent on temperature, conditions of formation, etc

α stannic acid may be prepared by treating a soluble tin salt with alkalies, or by decomposing stannates with acids, or by hydrolyzing dilute solutions of tin salts The α acid is a white voluminous or colloidal precipitate, which, when dried, looks like broken bits of glass When moist, it reddens litmus and is peptized rather than dissolved by water The heat of formation for the compound $Sn,O_2,2H_2O$ is 133 49 Cals

[18] *Z anorg Chem*, 9 369 (1895), 12 436 (1896)
[19] *Monatsh*, 39 149 (1918)
[20] *Z anorg Chem*, 64 368 (1909), 74 207 (1912), 84 121 (1914)
[21] *Liebig's Ann*, 301 368 (1898)
[22] *J Phys Chem*, 26 654 (1922), 28 232 (1924), "Colloid Symposium Monograph," Wisconsin, Co-operative Publishing Co, 1923, p 38
[23] Beitrage zur Chemie der Zinnsauren vom Kolloidchemischen Standpunkt, Dissertation, Gottingen, 1913

as given by Thomsen, the heat of neutralization as a base (with HCl) is 3 11 Cals , and as an acid (with NaOH) is 9 56 Cals

Colloidal α stannic acid may be made in the same manner as silicic acid T Graham [24] found that when he dialyzed a solution of stannic chloride and an alkali, he obtained a gelatinous mass on the dialyzer As the salts diffused away, the jelly was again peptized by the small amount of free alkali remaining The liquid α acid is converted by heating to the β form Both in liquid form are remarkable for the ease with which they are peptized by minute additions of hydrochloric acids as well as salts Bellucci and Parravano [25] found that when potassium-stannate solutions, ice cooled, are decomposed by small amounts of hydrochloric acid, stannic hydroxide, $Sn(OH)_4$, or orthostannic acid, H_2SnO_3 H_2O, is formed, whose composition remains constant after extended drying

Freshly prepared α stannic acid is soluble in dilute mineral acids, but nitric-acid solutions gelatinize on standing The property of solution in acids is gradually lost with increasing age Stannic acid is soluble in, or is peptized by, solutions of alkalies, including ammonia The salts of α stannic acid behave as if it were dibasic, as K_2SnO_3 $3H_2O$ for example Stannic hydroxide diffuses in alkaline solution like stannous hydroxide $Sn(OH)_2$ is a feeble base, but when one OH radical is replaced by an ethyl or similar group, strong bases result

When stannic acid is precipitated from alkaline solutions, it absorbs basic dyes, precipitated from acid solutions, it absorbs acid dyes Weiser [26] has studied the colloidal action of stannic acid

α stannic acid has a strong tendency to pass into the β form The change is accelerated by heat β stannic acid can be prepared by oxidizing tin with nitric acid The nature of the product is different depending upon the acid concentration Engel [27] states that with one volume of concentrated nitric acid and two or more volumes of water, stannous nitrate is formed, with equal volumes of water and acid, a thick syrupy solution of stannic nitrate results, and with concentrated acid, stannic nitrate which readily decomposes and is precipitated, as it is not soluble in moderately concentrated nitric acid The tin nitrates are readily decomposed by hydrolysis, heating, drying, or standing, into metastannic or β stannic acid Ignition gives stannic oxide When the products from the action of nitric acid on tin are washed, it is found

[24] *Proc Roy Soc (London)*, 13 335 (1864), *J Chem Soc ,* 17 318 (1864), *Phil Trans ,* 156 399 (1866), *Phil Mag ,* (4), 32 401, 503 (1866), *Liebig's Ann ,* 13 146 (1835)
[25] *Atti accad Lincei,* (5), 13 ii 307 (1904), *Z anorg Chem ,* 45 142 (1905)
[26] "The Hydrous Oxides," New York, McGraw Hill Company, Inc , 1926
[27] *Compt rend ,* 124 765 (1897), 125 464, 651, 709 (1897)

that very large quantities of water are necessary to wash out the nitric acid which is adsorbed by the precipitate

Moist β stannic acid reddens litmus This may be due to its acidic nature, but it is more likely to be the effect of small amounts of adsorbed nitric or other acids Vignon [28] gives the heat of neutralization against potassium hydroxide as 11 5 Cals for air dried β stannic acid, and 5 3 Cals for material dried at 250° C β stannic acid is sparingly soluble in most acids and insoluble in nitric It absorbs small amounts of acids such as hydrochloric and sulfuric It dissolves in hydrochloric, but further additions of the acid precipitate the stannic acid Treadwell [29] gives the following reactions

$$(SnO(OH)_2)_5 + 10HCl = 10H_2O + (SnOCl_2)_5$$
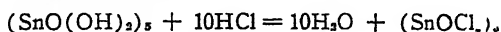
for the product insoluble in water, and

$$(SnOCl_2)_5 + 8H_2O \rightleftharpoons 8HCl + Sn_5O_2Cl_2(OH)_8$$

where the product is soluble in water, and

$$Sn_5O_2Cl_2(OH)_8 + 2HCl \rightleftharpoons 2H_2O + Sn_5O_2Cl_4(OH)_6$$
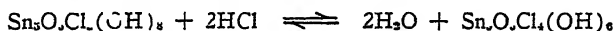
for the insoluble product formed upon further additions of acid When the water soluble material is boiled, hydrolysis takes place, as

$$Sn_5O_2Cl_2(OH)_8 + 2H_2O = Sn_5O_5(OH)_{10} + 2HCl$$
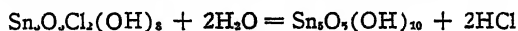
Berzelius states that the β stannic acid is less basic than the α acid Dilute alkalies dissolve β stannic acid, forming stannates of the formula $M_2Sn_5O_{11}$ 4H$_2$O, which do not crystallize readily An excess of alkali reprecipitates the β stannic acid Aqueous solutions of alkali carbonates or ammonia do not dissolve the β stannic acid

Stannic acid is peptized by a number of electrolytes It has considerable power of absorbing ions and electrolytes from solution In the case of hydrochloric acid, after equilibrium has been established, the concentration of the acid in the colloidal β stannic acid is often greater than that in the aqueous solution In the case of potassium chloride and nitrate, absorption is such as to cause equal concentrations of the electrolyte in the colloid and the solution In certain proportions a mixture of the hydrated oxides of iron and tin is soluble in dilute ammonia Weiser [30] showed that hydrated stannic oxide is peptized by the hydroxyl ion while hydrated ferric oxide is not Colloidal stannic oxide, or metastannic acid, adsorbs ferric oxide and carries it into colloidal solution as long as the tin compound is in excess Hydrated

[28] *Compt rend,* 108 1049 (1889), 109 372 (1889)
[29] "Kurzes Lehrbuch der analytischen Chemie," Leipzig, 1907, vol 1, p 215, London 1903 vol 1, p 220
[30] *Loc cit*

ferric oxide adsorbs the tin compound and tends to take it out of colloidal solution, so that while the former is present in large excess, none of the latter remains peptized Stannic oxide does not precipitate in the usual way from a solution of tin in nitric acid containing a suitable amount of iron Stannic oxide, when peptized by nitric acid, coagulates spontaneously since the aged oxide or stannic acid is neither peptized nor dissolved by nitric acid If freshly prepared colloidal stannic oxide be peptized by either ferric nitrate or a suitable mixture of this salt and nitric acid, aging or boiling the solution does not cause coagulation because the strongly adsorbed ferric ion exerts a stabilizing action If the ferric-ion concentration in the solution be too low, complete or partial coagulation of the peptized stannic acid takes place on stand- ing or boiling Chromic oxide and stannic acid gels mutually precipitate each other, the maximum effect occurring when equi-normal concentra- tions of the two solutions are mixed For further discussion of the rates of adsorption of various materials by colloidal stannic acid, the reader is referred to the extensive work given in the colloid chemistries

Spring [31] states that perstannic acid, $H_2Sn_2O_7$, is formed when a hydrated barium dioxide is added in excess to a hydrochloric-acid solution of stannic chloride, the turbid liquid dialyzed until barium chlo- ride no longer passes through the membrane, and the colloidal residue evaporated on a water bath Tanatar [32] stated that permonostannic acid, $HSnO_4 \cdot 3H_2O$, was formed when a solution of stannous chloride was treated with sodium carbonate, the precipitate triturated with an excess of 30 per cent hydrogen peroxide at 70° C, and the product dried in a desiccator When this product was further dried, it slowly lost water and oxygen and underwent partial decomposition in water, giving stan- nic acid and hydrogen peroxide He also prepared the salt potassium permonostannate, $KSnO_4 \cdot 2H_2O$, by the action of hydrogen peroxide on potassium stannate It has an alkaline reaction in water and decolorizes potassium permanganate when acidified with sulfuric acid When heated it is converted into potassium perdistannate, $K_2Sn_2O_7 \cdot 3H_2O$ Sodium salts are prepared in a similar manner They are all white amorphous powders

It is stated that when concentrated alkali stannate solutions are electrolyzed at low temperatures and low current densities, small amounts of perstannates are formed as a result of anodic oxidation The addition of alkali fluorides increases the rate of formation, but the final equilibrium of the perstannate formation is not altered The yield

[31] *Bull soc chim* (3), 1 180 (1889)
[32] *Ber*, 38 1184 (1905)

is small, inasmuch as considerable of the perstannate formed decomposes The yield diminishes rapidly as the temperature of electrolysis rises Decomposition of the perstannates yields stannates

STANNITES AND STANNATES

It has been previously pointed out that tin is amphoteric and can exist either in the hydroxide form in some of its compounds or in the acid form in which the summation formula is the same A large number of different stannates, being the salts of the stannic acids, are referred to in the literature They have been made either by the fusion of the oxides or the hydrates with alkali hydroxides or carbonates, or by the solution of the hydroxides or the tin acids in alkali solutions Depending on the method of preparation, the trihydrate $K_2Sn(OH)_6$, and the tetrahydrate $K_2Sn(OH)_6$ H_2O, and the pentahydrate $K_2Sn(OH)_6$ $2H_2O$ have been made The potassium salts are more soluble than the sodium and lithium salts The composition of the trihydrate agrees with the formula K_2SnO_3 $3H_2O$ They are colorless, shining, oblique, rhombic prisms often with the acute lateral edges truncated They are isomorphous with potassium hydroxyplatinate $K_2Pt(OH)_6$ They lose only small amounts of water at 100° C , but at 140° C moisture is copiously given off The dehydrated salt is hygroscopic Long continued drying decomposes the stannates into tin oxides and alkalies Crystalline stannates are readily soluble in hot and cold water On continued standing, however, they hydrolyze with the production of insoluble stannic acids

In its acid form, $Sn(OH)_4$ is stronger than as a base G E Collins and J K Wood [33] found the velocity constant of the reaction

$$K_2Sn(OH)_6 + 2H_2O = H_4Sn(OH)_6 + 2KOH$$
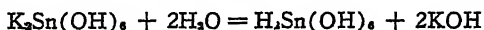
to be $k = 0 0188$, and the amount of free alkali present in a 0 128 N solution corresponds with a 13 per cent hydrolysis With a similar solution of stannic chloride, the hydrolysis was 94 per cent Frémy [34] found that aqueous solutions of stannates are precipitated by soluble salts α stannic acid is precipitated by the addition of acids to the stannates, this reaction even being shown to a limited extent by carbonic acid If carbon dioxide is introduced very slowly in contact with stannate crystals, monohydrated stannic oxide, seemingly amorphous, is formed Lead and copper precipitate tin from stannate solutions Sodium stannate is used in calico printing under the name of "preparing salts "

At low temperatures, concentrated solutions of sodium stannate free from alkali hydroxides furnish long prismatic crystals of the

[33] *J Chem Soc*, 121 441, 1122 (1922)
[34] *Ann chim phys* (3), 12 484 (1844), (3) 23 399 (1847)

decahydrate Na_2SnO_3 $10H_2O$ These are six sided tablets belonging to the trigonal system Mixter [35] gives the following thermal values

$$2Na_2O_2 + Sn = Na_2SnO_3 + Na_2O + 138 \text{ Cals}$$
$$(Na_2O,Sn,O_2) = 172 6 \text{ Cals}$$
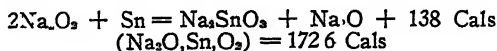
and with crystalline stannic oxide

$$(Na_2O,SnO_2) = 354 \text{ Cals}$$
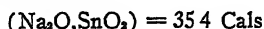
and with amorphous oxide, 371 Cals In many respects the sodium salts are similar to the potassium stannates Zocher [36] prepared lithium stannate Li_2SnO_3 $3H_2O$ or $Li_2Sn(OH)_6$ and the pentahydrate $Li_2Sn(OH)_6$ $2H_2O$ Ammonium β stannate has not been made, inasmuch as the β stannic acid is insoluble in ammonia Frémy [37] stated that a number of β stannates were produced with varying proportions of K_2O and SnO_2 but these have been regarded by van Bemmelen [38] as adsorption products since they have not been obtained in the crystalline state The supposed β stannate, K_2O $5SnO_2$ $4H_2O$, prepared by the action of potassium hydroxide on a solution of β stannic acid in potassium hydroxide appears as a horny, translucent colloid when dried It cannot be crystallized, but is apparently soluble or at least dispersable in water α stannates are formed when it is heated with concentrated alkalies It is completely soluble in water after dehydration at 130° Similar sodium β stannates have been prepared There have been reported in the literature a large number of so-called salts containing alkalies, tin oxides, and water in various proportions The existence of a great number of them is doubtful

It is thought that the opacity produced in glass and enamels by stannic oxide is caused by the formation of compounds of potassium and sodium carbonate and stannic oxide in various proportions Zulkowsky [39] regards $K_2Sn_2O_5$ as potassium mesodistannate Moberg [40] stated that he prepared ammonium α mesodistannate, $(NH_4)_2Sn_2O_5$ nH_2O, as a viscous mass, by evaporating a saturated solution of stannic hydroxide in aqueous ammonia over sulfuric acid

Copper stannates are formed when copper salts are treated with stannates They are yellowish-green precipitates which, if kept out of contact with air, become yellow, or, on exposure to the air, form mixtures of copper hydroxide and stannic acid, or mixtures of copper and tin oxides Moberg prepared green cupric α stannate, $CuSnO_3$ $3H_2O$

[35] *Am J Sci* (4), **27** 229 (1909)
[36] *Z Kryst*, **112** 1 (1920)
[37] *Ann chim phys* (3), **12** 484 (1844), (3), **23** 399 (1847)
[38] *Z anorg Chem*, **23** 124 (1900)
[39] *Chem Ind*, **22** 280 (1899), **24** 422 (1901)
[40] "Dissertatio de Stannatibus," Helsingfors, 1838, *Liebig's Ann*, **44** 261 (1842), *J prakt Chem* (1), **28** 231 (1843)

Ditte [41] produced small blue crystals by the addition of a solution of potassium stannate to an ammoniacal solution of a cupric salt until the precipitate failed to redissolve The product dissolved readily in aqueous ammonia and dark blue crystals were obtained which were sparingly soluble in cold water and formed a green solution with acids The material was assumed to be ammonium cupric α stannate

It is stated that silver α stannate, $Ag_2SnO_3 \cdot 2H_2O$, and silver β stannate, $Ag_2Sn_5O_{11}$, exist The β stannate, dried at 80° C, has a deep blue-black color When heated it loses water and detonates The anhydrous material is insoluble in dilute acids, but warm concentrated nitric acid dissolves out the silver, leaving metastannic acid The α stannate is soluble in dilute nitric acid but insoluble in water When heated it loses water and becomes insoluble in dilute acids

Calcium α stannate has been formed by fusing molten proportions of calcium and stannic oxides It crystallizes in small transparent crystals as plates and cubes of more or less altered octahedra It is stated that calcium stannates are formed by the addition of calcium salts to solutions of stannates Strontium, barium, and magnesium stannates are made in a similar manner References are found in the literature to the stannates of zinc, mercury, lead, and manganese, as well as the rose red crystals of cobalt α stannate, pale green cubic crystals of nickel α stannate, and salts of the precious metals such as platinum and palladium Many of these are true salts, but others are mixtures of oxides of the metals and tin A number of them are adsorption products of metallic salts by stannic acid or tin oxide, or of colloidal metals adsorbed by metastannic acid or stannic hydroxide The literature is exceedingly contradictory on the metal stannates

Chrome tin pink is developed when a mixture of stannic oxide and a small proportion of chromic oxide is calcined in the air at high temperatures If some calcium carbonate is present, the color develops at a lower temperature It is probably related to the chrome-alumina crimson of the ruby in that finely divided chromic oxide is deposited on or adsorbed by the stannic oxide

HALIDES OF TIN AND RELATED COMPOUNDS

Aqueous hydrofluoric acid has relatively little action on tin even when warmed, but it readily dissolves stannous oxide to form crystals of stannous fluoride, SnF_2 When exposed to the air, the salt is transformed into stannic oxyfluoride, $SnOF_2$ The tin fluorides are easily

[41] *Ann chim phys*, (5), 27 167 (1882), (6), 30 282 (1893), *Compt rend*, 94 1114 (1882), 96 702 (1883), 104 172 (1887)

soluble in water but hydrolyze readily Hydrogen sulfide precipitates stannous sulfide from a solution of stannous fluoride containing some free acid Frémy [42] claimed that an excess of hydrofluoric acid and stannous oxide react to form hydrofluostannous acid, H_2SnF_4 or $2HF \cdot SnF_2$ Wagner [43] states that corresponding ammonium and potassium fluostannites are formed

Tin is not readily attacked by fluorine at ordinary temperatures, but at 100° C white stannic fluoride is formed with incandescence The compound may also be formed by the addition of stannic chloride to anhydrous hydrofluoric acid at low temperatures After removal of the excess hydrogen chloride and stannic chloride, the residue has the composition $SnCl_4 \cdot SnF_4$, which later decomposes with the evolution of stannic chloride Stannic fluoride sublimes at 750° C The salt is very hygroscopic When its solutions are boiled or allowed to stand, hydrated stannic oxide is deposited, although stannic fluoride is more resistant to hydrolysis than stannic chloride Stannic fluoride reacts with a number of substances and has similar effects on organized vegetable matter as the other tin halides

Complex fluostannates, isomorphous with the fluosilicates, exist, being salts of the hypothetical hydrofluostannic acid, H_2SnF_6 These salts, however, may also be considered as double fluorides Ammonium, lithium, sodium, potassium, rubidium, and cesium salts are known and have been studied Somewhat less is known of the copper, silver, calcium, strontium, barium, magnesium, zinc, cadmium, manganese, nickel, and lead salts, although the crystallographic data for practically all of these as well as their solubilities have been determined

Analogous to the fluorides, two types of chlorides corresponding with the oxides exist,—stannous chloride $SnCl_2$, and stannic chloride $SnCl_4$. Each of these forms hydrates and hydrochlorides

Tin dissolves readily in warm hydrochloric acid to form stannous chloride, and if a solution of stannous chloride in dilute hydrochloric acid be evaporated and cooled, crystals of dihydrated stannous chloride, $SnCl_2 \cdot 2H_2O$, are formed This material is the so-called "tin salt" of commerce Stannous oxide is readily soluble in hydrochloric acid to form the chloride The physical properties of the stannous chlorides are given in Table 12

Engel [44] found the solubility of stannous chloride in water is increased by a large proportion of hydrochloric acid The anhydrous salt is readily dissolved by alcohol and to a less extent by ether It is soluble

[42] *Ann chim phys* (3), 47 37 (1856)
[43] *Ber*, 19 896 (1886)
[44] *Ann chim phys* (6), 17 338 (1889), *Compt rend*, 106 1398 (1888)

TABLE 12

PHYSICAL PROPERTIES OF STANNOUS CHLORIDE

Boiling point	603–606° C	
Electrical conductivity		
Solid chloride, 222° to 244° C	0 002 to 0 014 mho	Klemm and Biltz [1]
Molten chloride,		
263° C	0 89 mho	" " "
302° C	1 12 "	" " "
314° C	1 18 "	" " "
353° C	1 42 "	" " "
411° C	1 72 "	" " "
Heat of formation		
$Sn,2HCl_{gas}$	36 4 Cals	Thomsen [2]
Sn,Cl_2 (with solid stannous chloride)	80 79 Cals	"
$Sn,Cl_2,2H_2O$ at 18° C	5 72 Cals	"
Heat of solution		
$SnCl_2 2H_2O + Aq$	53 7 Cals	"
$(SnCl_2,Aq)$	350 0 Cals	"
In 1% HCl	0 9 Cal	Biltz and Fischer [3]
Heat of vaporization	46 84 Cals	Regnault [4]
Mol heat of vaporization at 622 8° C and 371 4° C	21 100 cals	Maier [5]
Magnetic susceptibility		
Per gram	$-0 334 \times 10^{-6}$	
Per mol	$-0 055 \times 10^{-6}$	
Mass units at 18° C	$-0 29 \times 10^{-6}$	
Mass units	$-0 07 \times 10^{-6}$	Quincke [6]
Melting point	246 8° C	Kendall, Crittenden and Miller [7]
Solubility		
In H_2O at 0° C	83 9 parts in 100 of H_2O	Engel [8]
at 15° C	269 8 grams per 100 grams H_2O	
In formic acid (95%) at 19° C	4 1 grams per 100 grams acid	Aschan [9]
In acetone, saturated, at 18° C	1 gram per 1 8 grams acetone	Naumann [10]
$SnCl_2 2H_2O$		
In ethyl acetate		
at —2° C	31 2 grams in 100 parts	von Laszczynsky [11]
22° C	35 5 grams in 100 parts	" "
82° C	73 4 grams in 100 parts	" "
Specific heat, 20° to 99° C	0 10162	Regnault [4]

[1] *Z anorg Chem*, 152 225, 267 (1926)
[2] *J prakt Chem*, (2), 14 429 (1876), (2), 18 1 (1878)
[3] *Z anorg Chem* 129 1 (1923)
[4] *Ann chim Phys*, (3), 1 129 (1841), "Relation des experiences entrepris pour determiner les principales lois physiques et les donnees numeriques qui entrent dans le calcul des machines a vapeur," Paris, 1847
[5] "Vapor Pressures of the Common Metallic Chlorides," *Bur Mines Tech Paper*, 360, (1925), p 38
[6] *Wied Ann*, 24 347 (1885), 34 401 (1888)
[7] *J Am Chem Soc*, 45 963 (1923)
[8] *Ann chim phys*, (6), 17 338 (1889), *Compt rend*, 106 1398 (1888)
[9] *Chem Ztg*, 37 1117 (1913)
[10] *Ber*, 37 3601, 4336, 4609 (1905)
[11] *Ber*, 27 2285 (1894)

TABLE 12—*Continued*

Specific gravity at 24° C	2 634			F W Clarke [12]
Thermal expansion coefficient	0 000319			Lorenz and Herz [13]
Vapor density at 619–697° C	12 96			V and C Meyer [14]
Vapor pressure				
at 372 7° C	10 2 mm Hg			Maier [5]
447 8° C	56 4	"	"	"
499 4° C	116 6	"	"	"
536 2° C	205 3	"	"	"
563 1° C	346 9	"	"	"
596 6° C	537 5	"	"	"
617 5° C	706 3	"	"	"
633 9° C	882 0	"	"	"
641 0° C	972 4	"	"	"

[12] *Am J Sci* (3) 14 281 (1877)
[13] *Z anorg Chem*, 145 88 (1925), 147 135 (1925)
[14] *Z phys Chem*, 12 1195 (1879)

in pyridine, and to the extent of almost 16 per cent in methyl acetate, and almost twice as much in ethyl acetate, in which the solubility increases rapidly with the increase of temperature

Anhydrous stannous chloride is fairly stable in the air, but it shows appreciable oxidation after continued exposure The salt is converted into oxychlorides by oxygen If aqueous solutions are exposed to the air, both hydrolysis and oxidation occur with the formation of complicated materials consisting of mixtures of oxychlorides and metastannic acid Scheurer-Kestner [45] showed that oxygen is absorbed by a dilute solution of stannous chloride to form stannic chloride and stannic acid, but that with concentrated solutions, oxygen is not absorbed The oxidation of stannous chloride solutions is promoted by the presence of rubber, sulfur, ferrous and cupric sulfates, but is retarded by manganous salts, some of the alkaloids, and potassium cyanides The oxidation of stannous chloride simultaneously induces the oxidation of sodium arsenite, formate, and oxalate if these are present in the solution Easily oxidizable substances such as hydroquinone, sugars, glycerol, and a number of organic substances retard the oxidation of stannous salts by air

Aqueous solutions of stannous chloride are hydrolyzed when heated to 200° C in sealed tubes, with the resulting formation of yellow flocculent oxychloride A large number of investigators have studied the hydrolysis of stannous chloride A number of compounds containing various proportions of SnO, $SnCl_2$, and H_2O are supposed to exist

Chlorine oxidizes stannous chloride to stannic chloride The reaction, according to Berthelot,[46] is

[45] *Compt rend*, 52 531 (1861), *Ann chim phys* (3), 58 471 (1860)
[46] *Ann chim phys* (5) 15 200 (1878), "Thermochimie," Paris, 1897, vol 2, p 154

$$SnCl_2 + Cl_2 = SnCl_4 \text{ } _{1q} + 48 8 \text{ Cals}$$

and in aqueous solution,

$$SnCl_{2 \text{ } aq} + Cl_2 = SnCl_{4 \text{ } aq} + 72\text{-}78 2 \text{ Cals}$$

Bromine causes the formation of stannic salts in aqueous solution, while the dichlorodibromide is formed with the anhydrous stannous chloride At ordinary temperatures iodine has little oxidizing power, but when it comes in contact with stannous chloride, the salt gradually becomes pale red If a solution of stannous chloride is saturated with hydrochloric acid at 0° C and cooled to —40° C , crystals of the addition compound $SnCl_2$ HCl are formed The salt melts at —27° C S W Young,[47] from his studies of the electrical conductivity of a solution of stannous chloride in hydrochloric acid, believed that the compound $SnCl_2$ 2HCl was also formed Stannous chloride reduces hypochlorous acid and potassium chloride, the latter being catalyzed by vanadic oxide It also reduces antimony pentachloride

Hydrogen sulfide precipitates stannous sulfide from solutions of stannous salts Hering[48] found that stannous chloride is oxidized by sulfur dioxide according to the following equation

$$6SnCl_2 + 2SO_2 + 8HCl = 5SnCl_4 + SnS_2 + 4H_2O$$
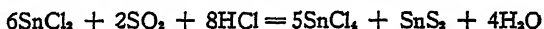
This agrees with the work of Fink and Mantell on the oxidation of stannous oxide by sulfur dioxide, discussed elsewhere The compounds resulting from the action of sulfur dioxide and stannous chloride depend upon the proportions of the components entering into the reaction Fedoroff[49] showed that the sulfides of arsenic, copper, antimony, bismuth, and platinum are formed when their salts are treated with a hydrochloric-acid solution of stannous chloride and sulfur dioxide, while all the tin remains in solution as stannic chloride The action of concentrated sulfuric acid on a cold solution of stannous chloride produces only a little hydrochloric acid, but gives rise to stannic sulfate, stannic chloride, sulfur dioxide, hydrogen sulfide, and a little free sulfur, as a result of the marked reducing action of stannous chloride Ordinarily stannous salts are stronger reducing agents than sulfur dioxide

Ammonia and alkalies precipitate the hydroxides when caused to react with stannous chloride When treated with liquid ammonia, stannous chloride forms a yellow compound of low solubility Persoz[50] found that warm stannous chloride absorbs gaseous ammonia to form

[47] *J Am Chem Soc ,* 23 21, 450 (1901)
[48] *Liebig's Ann.* 29 90 (1839)
[49] *Z Chem* (2), 5 15 (1869).
[50] *Ann chim phys* (2), 44 315 (1830).

the compound $SnCl_2NH_3$ A number of supposed compounds of stannous salts and hydrazine are stated to exist Stannous chloride reduces nitric acid to form stannic chloride, stannic acid, and the oxides of nitrogen The reaction is accelerated by the presence of vanadic oxide The reduction reactions vary widely according to the concentration of the nitric acid employed Stannous chloride can be used as a reducing agent for the conversion of colloidal metallic oxides, such as those of antimony and arsenic, as well as for the reduction of bismuth nitrate to the black lower oxides or to the metal It also has marked reducing action on many organic compounds, such as the conversion of the nitro compounds to the amides

Tin is precipitated from stannous salts by the more electropositive metals, such as magnesium, zinc, cadmium, and aluminum Pleischel [51] found that lead precipitates tin quantitatively from stannous solutions, while Reinsch [52] found that copper precipitates tin as a greyish-black powder from solutions strongly acid with hydrochloric acid

In the presence of tartaric acid, solutions of stannous salts do not yield precipitates when treated with hydroxides A number of oxidizing agents, such as the nitrates and chlorates, convert stannous salts to stannic compounds and oxides Chromic acid is reduced to a chromic salt, while tungstic and molybdic acids form the lower blue oxides when treated with stannous salts The analytical reaction of the reduction of mercuric chloride to white calomel is well known With silver salts, metallic silver is precipitated, and in the case of gold salts, the colloidal metallic gold known as "purple of Cassius" is formed

A large number of complex double chlorides are formed by the interaction of stannous chloride and salts of other metals These compounds, as well as their best known properties, are given in the table of salts

Stannic chloride is often stated to be the discovery of Libavius in 1605, when he obtained the material by distillation of a mixture of tin or tin amalgam and mercuric chloride The fuming liquid was named *spiritus fumans Libavii* The material is made commercially by the direct action of chlorine on tin The reaction is highly exothermic and is discussed in some detail in the section of this book dealing with the detinning of tin plate scrap The commercial operation takes place at low temperatures The reaction is catalyzed by sulfides and sulfur compounds A large number of methods, mostly of the laboratory type, are given in the extensive literature on the subject of stannic chloride

[51] *Sitzb Akad Wien* **43** 555 (1861)
[52] *J prakt Chem,* (1) 24 248 (1841)

Stannic chloride forms hydrates with varying quantities of water, depending upon the amount of water with which it is allowed to come in contact The phase rule diagram of the stannic chloride-water system has been often studied, but as a result of the formation of oxy salts, there is still considerable disagreement in reference to the system Difficulty is found in the commercial preparation of solutions of stannic chloride Dilution can be done only under carefully controlled conditions The physical properties of stannic chloride are given in Table 13

TABLE 13

PHYSICAL PROPERTIES OF STANNIC CHLORIDE

Boiling point at 760 mm	114° C	Kendall, Crittenden, and Miller [1]
Critical density	0 732–0 743	S Young [2]
Critical pressure	28,080 mm	" "
Critical temperature	318 7° C	" "
Critical volume	1 347	" "
Cubical expansion coefficient, 0° to 100° C	0 00129977	Pierre [3]
Dielectric constant at 22° C	3 2	Schlundt [4]
	2 0	Mathews [5]
Ebullioscopic constant	0 515 to 0 65	de Kolossowsky [6]
Electric conductivity	nil	Coldridge [7]
Freezing point	— 33° C	
Heat of formation		
Sn,2Cl₂	127 25 Cals	Thomsen [8]
SnCl₃ aq Cl₂	76 03 Cals	"
Heat of fusion at melting point	8 42 cals per gram	Latimer [9]
Heat of solution in H₂O	29 92 Cals	Thomsen [8]
Heat of vaporization	32 6 cals	Hammick [10]
Total from 0° C to temp of vaporization	46 838 Cals per kg	Regnault [11]
Internal pressure of liquid	1184 atmospheres	Schuster [12]
Magnetic susceptibility	—0 18 × 10⁻⁶ mass units	Quincke [13]
Specific gravity 0° C (H₂O at 4° C = 1 00)	2 2788	
Aqueous solution at 15° C		
10% SnCl₄	1 082	Gerlach [14]
20% "	1 174	"
30% "	1 279	"
40% "	1 404	•

Heat of formation: $Sn, 2Cl_2$, $SnCl_3 \text{ aq } Cl_2$. Magnetic susceptibility -0.18×10^{-6} mass units.

[1] *J Am Chem Soc*, 45 963 (1923)
[2] *J Chem Soc* 59 911 (1891), "Fractional Distillation," London, Macmillan, 1903, p 12, *Proc Dublin Sci Soc* (2), 12 428 (1910), *Phil Mag* (5), 34 505 (1902)
[3] *Ann chim phys* (3), 19 193 (1847), (3), 20 1 (1847)
[4] *J Phys Chem*, 5 503 (1901)
[5] *J Phys Chem*, 9 641 (1905)
[6] *J chim phys*, 23 353 (1926)
[7] *Phil Mag* (5), 29 383 (1890)
[8] "Thermochemische Untersuchungen," Leipzig, 3 327 (1883)
[9] *J Am Chem Soc*, 44 90 (1922)
[10] *Phil Mag* (6) 44 590 (1922)
[11] 'Relations des experiences entrepis, pour determiner les principales lois et les donnees numeriques qui entrent dans le calcul des machines a vapeur," Paris, 1862, p 203, *Mem Acad*, 21 1 (1847), *Ann chim phys* (3) 9 322 (1843)
[12] *Z Elektrochem*, 32 191 (1926)
[13] *Wied Ann*, 24 347 (1885), 34 401 (1888)
[14] *Dingler's J*, 178 49 (1865)

TABLE 13—*Continued*

50% SnCl₄	1 556	Gerlach [14]
60% "	1 743	"
70% "	1 943	"
100% "	2 234	"
Specific heat		
Vapor, for equal weights	0 0939	Regnault [11]
Vapor, for equal volumes	0 8416	"
Liquid 14° to 98° C	0 1476	"
Aq solution 10° to 15° C	0 1402	"
Specific volume	131 07	Thorpe [15]
Vapor pressure (p) at ° C		
—10	2 78 mm Hg	S Young [2]
0	5 53 " "	" "
10	10 33 " "	" "
20	18 58 " "	" "
40	50 82 " "	" "
60	122 2 " "	" "
80	256 7 " "	" "
100	496 0 " "	" "
120	895 4 " "	" "
130	$p \times 10^{-3} = 1\,171$	" "
200	" $= 5\,145$	" "
250	" $= 11\,514$	" "
310	" $= 25\,079$	" "
319 35	" $= 28\,079$	" "

[15] *Proc Roy Soc (London)*, 24 283 (1876), *J Chem Soc*, 37 331 (1880)

The vapor pressure of stannic chloride is quite appreciable at low temperatures When exposed to the air, the material fumes markedly It has been employed in times of war for the formation of smoke screens to cover military tactics It has been superseded for this use by compounds of silicon, titanium, and phosphorus It finds extensive application in the textile industries, particularly in silk weighting

Stannic chloride forms a number of addition compounds analogous to the complex stannous chlorides Upon hydrolysis, a large number of complicated compounds are formed These have been widely studied, but the results are confusing and show little concordance At low temperatures, stannic chloride absorbs large quantities of chlorine, with considerable increase in volume and lowering of the freezing point The freezing-point curve of mixtures of chlorine and stannic chloride is shown in Figure 89 There is no evidence of the existence of complex salts Hydrogen sulfide precipitates stannic sulfides from stannic salts only with difficulty after long periods of treatment Stannic chloride forms compounds with materials such as sulfur monochloride, S_2Cl_2. These fume more strongly in air than does stannic chloride In a current of hydrochloric acid, the compound sublimes with very little decomposition at 30° C It dissolves in water without the separation of sulfur to form stannic chloride, hydrochloric, and sulfuric acids

Rose [53] states that stannic chloride absorbs appreciable amounts of sulfur trioxide without giving off sulfur dioxide Weber [54] states that he formed stannic selenoxychloride, $SnCl_4 \cdot 2SeOCl_2$ Sulfuric acid has practically no effect on stannic chloride Davy [55] found that stannic chloride absorbs dry ammonia at ordinary temperatures, with the development of heat, forming a white solid When sublimed, the material corresponds to the formula $SnCl_4 \cdot 2NH_3$ Exposed to the air, it gives off white pungent fumes It dissolves completely in water

Nitric acid attacks stannic chloride with the formation of chlorine, nitrogen oxides, and stannic acid A number of compounds are supposed
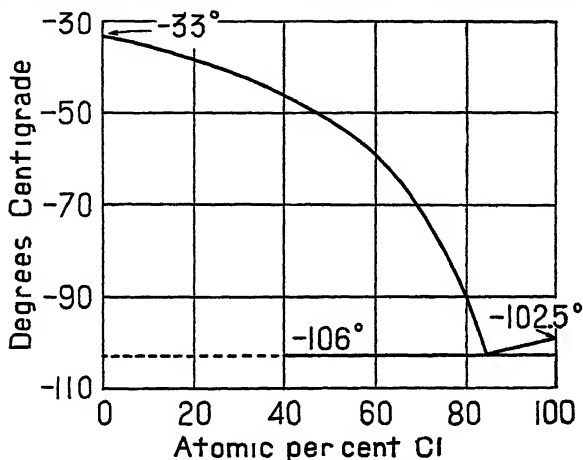
FIG 89 —Freezing-point curve of mixtures of chlorine and stannic chloride

to be formed by the interaction of stannic chloride and the oxides of nitrogen, but many of these are unconfirmed Stannic chloride absorbs phosphine, according to Rose,[56] to form a fuming hygroscopic solid of the formula $3SnCl_4 \cdot 2PH_3$ The material decomposes in carbon dioxide at 100° C Stannic chloride mixes with phosphorus trichloride without chemical combination, but forms an addition compound with phosphorus pentachloride Phosphorus pentachloride reacts with tin to form stannic chloride The reactions of the phosphorus and the stannic compounds have been studied by Casselmann [57]

Stannic chloride reacts with alcohol and organic compounds of the same nature to form the corresponding chlorides and stannous oxy-

[53] *Pogg Ann* 16 339 (1829), 24 339 (1832), 42 517 (1837), 44 320 (1838)
[54] *Sitzb Akad Berlin*, 1865, p 154
[55] *Phil Trans*, 102 169 (1812)
[56] *Pogg Ann*, 24 159 (1832)
[57] *Liebig's Ann*, 83 257 (1852), 91 242 (1854), 98 213 (1856)

chloride In general it is an oxidizing agent toward organic materials, and a number of complex salts are known Stannic chloride is reduced by potassium metal in toluene solution It reacts with mercury to oxidize the mercury, and is itself reduced to stannous chloride It forms a large number of complex salts with the metal chlorides Biron [58] prepared the addition compounds of stannic chloride with the chlorides of calcium, strontium, beryllium, magnesium, manganese, iron, nickel, cobalt, and zinc, but not of barium, cadmium, silver, copper, lead, and thallium The presence of the chlorides of those elements which form addition compounds retards the speed of hydrolysis of stannic chloride No one metal salt is more effective than the others

The pink salt used by the calico printer is a double chloride of tin in the stannic form, and ammonia, having the formula $SnCl_4 \cdot 2NH_4Cl$ The salt crystallizes in octahedra of the cubical system

Stannous bromide has been prepared by heating tin in an atmosphere of hydrogen bromide An oily liquid condenses close to the hot zone Upon cooling, it freezes to a gray mass Stannous bromide forms a pale yellow crystalline material consisting of hexagonal columns belonging to the rhombic system The material is oxidized by the same reagents as affect stannous chloride Its analytical reactions are quite analogous to those of the chlorides It hydrolyzes readily and forms addition compounds with ammonia and the bromides of other metals

Tin burns in an atmosphere of bromine to form stannic bromide The material is a white crystalline substance which may be sublimed without decomposition The crystals are rhombic pyramids with a melting point of $31°$ C The salt is fairly stable when heated Its reactions are quite analogous to those of stannic chloride With water it forms hydrates and hydrolyzes fairly readily to form hydroxy compounds of the same nature as those formed by stannic chloride It does not react with liquid hydrogen sulfide at $-78.5°$ C , nor does it form compounds with sulfur dioxide below the melting point of sulfur dioxide, $-72°$ C In the system $SnBr_4 \cdot SO_2$, the critical solution temperature is $48.6°$ C and there is a eutectic at $16.3°$ C on the stannic bromide side of the percentage solubility in sulfur dioxide curve Molten stannic bromide dissolves iodine readily as well as sulfur When dissolved in liquid sulfur dioxide, it is not a good electrical conductor Balard [59] states that stannic bromide dissolves readily in sulfuric acid without perceptible decomposition, to form an oily liquid Analogous to stannic chloride, the bromide absorbs ammonia to form an addition compound, $SnBr_4 \cdot 2NH_3$

[58] *J Russ Phys Chem Soc*, 36 489 (1904), 37 994, 1036 (1905)
[59] *Ann chim phys* (2), 32 337 (1826)

With nitric acid the vapor of bromine is given off vigorously Walden [60] found that stannic bromide is soluble in arsenic tribromide

Fine colorless prisms of needle-like crystals are obtained when very concentrated solutions of stannic bromide are saturated with hydrobromic acid The material is regarded as the addition compound $SnBr_4$ $2HBr$ $8H_2O$ The salt is very deliquescent and readily gives off hydrogen bromide The crystals fume in air

A series of addition compounds with the bromides of other metals is known Those which have been studied include the ammonium, cesium, rubidium, potassium, sodium, lithium, calcium, strontium, magnesium, manganese, iron, cobalt, and nickel double bromides

A number of stannic bromochlorides, or mixed salts containing both chlorine and bromine, have been reported They are made ordinarily by the addition of bromine to stannous or stannic chlorides, or by the addition of chlorine to stannous or stannic bromides

Analogous to the other halides, tin forms stannous and stannic iodides Mixtures of the two are obtained when tin filings are heated with iodine They can be separated by sublimation, inasmuch as stannic iodide volatilizes at 180° C and stannous iodide remains fixed at red heat Stannous iodide can be prepared by the reducing action of tin on stannic iodide in a sealed tube under prolonged heating at 360° C Stannous iodide is precipitated by treatment of stannous chloride with iodine, a mixture of stannous iodide and chloride as well as stannic chloride remaining in solution Metallic iodides, when added to solutions of stannous chloride, precipitate yellow-reddish crystalline tufts of stannous iodide, if the mixture is warmed, the crystals are yellow-red needles When crystallized from its aqueous solution, the iodide contains two molecules of water When dried over sulfuric acid, the monohydrate is formed Exposure to sunlight changes the yellow iodide to the red form, the reverse change taking place in the darkness The yellow form is considered to be the stable modification at 100° C

Adsorption compounds with ammonia are formed by the iodides in a manner analogous to those formed by the other halides Similar oxy salts result from hydrolysis Stannous iodide is soluble in a solution of stannous chloride Complex addition compounds are formed with hydrobromic acid and the metallic iodides, as well as complex chloroiodides and bromoiodides, analogous to the complex compounds formed by the other halides Complex double iodides with ammonium, sodium, potassium, rubidium, cesium, barium, and strontium have

[60] *Z phys Chem*, 43 385 (1903), *Z anorg Chem*, 29 377 (1902)

been studied Young [61] prepared yellow-red prisms of the addition compound $SnCl_4$ SnI_2 by the action of iodine chloride on stannous chloride A number of replacement compounds, in which chlorine or bromine replaces part of the iodine in the stannous and stannic iodides, are known

When a warm solution of iodine in carbon bisulfide is allowed to act on tin metal, red, singly refracting crystals are obtained which belong to the rhombic system According to Henry [62] the salt sublimes at 180° C, forming reddish-yellow needles The stannic iodides are hydrolyzed in aqueous solution The salt is soluble to the extent of 140 parts per 100 in carbon bisulfide, and readily dissolves in chloroform alcohol, ether, and benzene, forming compounds with all of these except chloroform Biltz and Kuenecke [68] observed no reaction with liquid hydrogen sulfide at −78 5° C A number of complex addition compounds are formed. Those of importance are given in the appendix of the table of solubilities of tin compounds Analogous to the other halides, the stannic iodides react with ammonia to form addition compounds whose formulæ vary with the concentration of the ammonia employed and the quantity used in the reaction Stannic iodide dissolves in stannic chloride and antimony chloride Chloro- and bromoiodides, obtained by the reaction of chlorine and bromine on stannous iodide, are formed

SULFIDES OF TIN

Tin forms two well-established sulfides, the stannous form, SnS, and the stannic compound, SnS_2 Many statements as to the formation of hydrated forms of these sulfides are found in the literature, but few of them have been confirmed Stannous sulfide is formed when a mixture of sulfur and tin is heated above the melting point of the metal, or when a stannous salt is caused to react with hydrogen sulfide in aqueous solution At red heat, stannic sulfide decomposes into stannous sulfide and sulfur Stannous sulfide melts at 880° C, passes into a viscous liquid at 950° C, and becomes limpid again at nearly 1100° C

Reinsch [64] found that if a solution of 1 part of stannous chloride in 100 parts of water and 15 parts of hydrochloric acid be treated with hydrogen sulfide, all the tin is precipitated at once, but if 25 parts of acid be used, precipitation occurs only after a considerable time interval, and if 40 parts of acid be used, no tin sulfide is precipitated until the

[61] *J Am Chem Soc* 19 845, 851 (1897)
[62] *Phil Mag* (3), 5 354 (1845), *Phil Trans*, 135 363 (1845)
[63] *Z anorg Chem*, 147 171 (1925)
[64] *J prakt Chem* (1), 13 132 (1838)

solution is diluted with water The physical properties of stannous sulfide are given in Table 14

TABLE 14

PHYSICAL PROPERTIES OF STANNOUS SULFIDE

Boiling point	1230° C	International Critical Tables, Vol 1
Melting point	880° C	Pelabon [1]
Specific gravity	5 080	International Critical Tables, Vol 1

[1] *Compt rend*, 142 1147 (1906), *Ann chim phys* (8) 17 526 (1909)

When roasted in air or oxygen, stannous sulfide is converted into stannic oxide Colloidal solutions of stannous sulfide are oxidized in sunlight and air with the formation of colloidal sulfur Stannous sulfide is very sparingly soluble in water to the extent of $0 14 \times 10^{-6}$ gram molecular weights per liter of water at 18° C Steam oxidizes the sulfide to hydrogen sulfide and stannic oxide The material is oxidized by hydrogen peroxide in alkaline solution with the formation of a sulfostannate At low temperatures, chlorine reacts on the compound to form stannic chloride and sulfur tetrachloride Hydrochloric acid gas at ordinary temperatures converts the sulfide into the chloride with the formation of hydrogen sulfide Stannous sulfide is not affected by sulfurous acid It is not ordinarily dissolved by metallic sulfides when solutions of these are less than 20 per cent, but more concentrated solutions gradually form metallic tin and sulfostannates Stannous sulfide is readily soluble in solutions of alkali metal or ammonium polysulfide Nitric acid readily oxidizes the amorphous sulfide to stannic oxide, but the crystalline form is but slowly attacked Phosphine is reduced by warm stannous sulfide, with the formation of hydrogen sulfide and phosphorus Perkin [65] found that some preparations of precipitated stannous sulfide readily dissolve in alkalies With concentrated caustic solutions, tin and alkali stannates and sulfostannates are formed Fusion of stannous sulfides with sulfur, carbon, and sodium carbonate converts the salt into a soluble alkali sulfostannate Potassium cyanide, especially when fused and in the liquid form, reduces stannous sulfide to tin Schurmann [66] showed that stannous sulfide is completely converted into the sulfate when heated with a solution of either copper or cadmium sulfate, but not by solutions of zinc sulfate Raschig [67] found that a solution of cuprous chloride dissolved in sodium chloride reacts with stannous sulfide to form cuprous sulfide and stannous chloride, and a boiling dilute solution of cupric chloride causes the formation

[65] *J Soc Chem Ind*, 20 425 (1901)
[66] *Liebig's Ann*, 249 341 (1888)
[67] *Ber*, 17 697 (1884), *Liebig's Ann*, 228 19 (1885)

of cuprous sulfide and stannic chloride Mourlot [68] states that stannous chloride is volatilized as the result of the heating of magnesium chloride and stannous sulfide in an electric furnace Stannous sulfide dissolves in molten glass with scarcely any color effect

Stannic sulfide in the form of mosaic gold was largely used in the eighteenth century as a paint pigment It was prepared by heating a mixture of tin, sulfur, ammonium chloride, and mercury At the present day, its application as a bronzing powder for wood, metals, and wallpaper is decreasing, inasmuch as it is being displaced by cheaper "bronze powders" made of metal Stannic sulfide can be made by the fusion of stannous salts with excess sulfur The color of the resulting product varies considerably as a result of different proportions Amorphous or colloidal stannic sulfide is produced when hydrogen sulfide is passed into an acidic solution of stannic chloride, or into water in which freshly precipitated stannic hydroxide is suspended It is also produced when a strong mineral acid is allowed to act on an aqueous solution of a sulfostannate Schmidt [69] states that the egg-yellow precipitate obtained by the action of hydrogen sulfide on stannic chloride solutions contains SnS_2 when moist, but that it decomposes during drying, giving off hydrogen sulfide, and becomes dark brown Jorgensen [70] found that the precipitate produced by the action of hydrogen sulfide on a solution of metastannic acid in hydrochloric acid has a sulfur content which varies with the concentration of the acid and the salt, the time, and the temperature of action A large number of workers, notably Weiser [71] and his associates, have studied the colloidal stannic sulfides The physical properties of stannic sulfide are given in Table 15 In its

TABLE 15

PHYSICAL PROPERTIES OF STANNIC SULFIDE

| Specific gravity . | 4 5 | International Critical Tables |
| Specific heat, 12° to 95° C | 0 11932 | Regnault [1] |

[1] *Ann chim phys* (3), 1 129 (1841)

crystalline form, the material consists of golden yellow plates which are soft and feel like graphite The salt reacts with a number of compounds in manners analogous to the stannous sulfide reactions Chlorine converts it at ordinary temperatures to a brown liquid which solidifies to yellow crystals of $SnCl_4 2SCl_4$ It reacts at red heat with phosphorus pentachloride, producing stannic chloride and sulfophosphide

[68] *Compt rend*, 124 768 (1897), *Ann chim phys* (7), 17 537 (1899)
[69] *Ber*, 27 2739 (1894), *Kolloid Z*, 1 131 (1907)
[70] *Z anorg Chem* 28 140 (1901)
[71] "The Colloidal Salts," New York, McGraw Hill Book Company, Inc, 1928

and phosphorus sulfide and sulfochloride Sulfuryl chloride converts stannic sulfide into stannic chloride and sulfur Aqueous alkalies dissolve the sulfide with the formation of stannates and sulfostannates Solutions of alkali sulfides, ammonium sulfides, and polysulfides dissolve stannic sulfide, forming sulfostannates A number of sulfochlorides are formed by the action of chlorine on stannic sulfide Analogous sulfohalides are formed by the action of iodine and bromine on the tin sulfides Stannic sulfoiodide is soluble in carbon bisulfide and chloroform Alcohol separates out the sulfur, and the tin and iodine dissolve as stannic iodide

Stannic sulfide unites with the more basic sulfides of the other elements to form a series of sulfostannates or thiostannates These are regarded as the salts of sulfometastannic acid, H_2SnS_3, or of sulforthostannic acid, H_2SnS_4, in which sulfur has replaced the oxygen of the stannic acids By themselves the acids are not known, being definitely hypothetical and existing only in stable form as their salts When mineral acids are caused to act on the thiostannates, tin sulfide is produced but not the thiostannic acids The analytical separation of tin from copper, mercury, and cadmium depends upon the formation of the sulfostannates as the result of the solution of the tin sulfides in alkali polysulfides The sulfostannates may also be considered as addition compounds of the sulfides Many of them are stable only in solution Although a large number have been described in the literature, only a few have been confirmed

The complex mineral sulfides, which are as yet unimportant as sources of tin metal, are described elsewhere in this volume under Tin Ores A number of the sulfostannates are given in the table of tin-salt solubilities

OTHER SIMPLE TIN SALTS

Tin forms stannous and stannic sulfate as the result of the action of sulfuric acid on tin metal and tin salts Freshly precipitated stannous hydroxide dissolves readily in dilute sulfuric acid, but the action of sulfuric acid on tin is slow In this connection the preparation of refining solutions for tin metallurgy is of interest, as discussed elsewhere. The tin sulfates, unless they be kept in contact with metallic tin in solution, show definite tendencies toward hydrolysis, although they are among the most stable of the tin salts A number of oxy salts are known, with widely varying composition Double sulfates, analogous to the alums, have been studied, the best known being those formed with sodium and potassium sulfates

TABLE 16

Physical Properties of Tin Salts

	Compound	M. W.	Sp G	M P °C	B P °C	Solubility—Grams per 100 cc			Crystal Form and Color
						Cold Water	Hot Water	Other Solvents	
1	SnBr₄	278 5	5 12¹⁷	215 5	617	sol	sol – decomp	sol alkalies, tartaric acid, acetic acid, ether and pyridene	yellow, rhombic
2	SnCl₄	189 6	2 63²⁴	246 8	603	83 9°	269 8¹⁵°		colorless, monoclinic
3	SnCl₄ 2H₂O	225 7	2 71¹⁵°	37 7	decomp	118 70°	∞		colorless, rhombic
4	SnCl₂ 2NH₄Cl 2H₂O	314 6	2 10⁸·⁹°			27 51⁶°		sol in dil min acids	colorless crystals
5	SnCl₂ SnO 4H₂O	396 4				sl sol	decomp	sol in chloride sols	white
6	SnCl₂ KCl H₂O	282 2	2 51			232 8²°	sol	sol in chloride sols	white, rhombic
7	SnCl₂ 2KCl 2H₂O	374 8				26 7⁸⁵°		KOH, fluorides	prisms
8	SnF₂	156 7				v sol	v sol	sol dil HCl, KOH	
9	SnI₂	372 5	5 29°	320 0	720 0	0 98²⁰°	4 03¹⁰⁰°	sol min acids, org acids	black, regular
10	SnO	134 7	6 90°	decomp	decomp	insol	insol	sol dil acids, alkalies	
11	Sn(OH)₂	152 7				0 00018	decomp		yellowish white amorph
12	SnP	149 7	6 56	decomp	decomp	insol	insol	sol HCl, insol HNO₃	white, amorphous
13	Sn₃(PO₄)₂	546 2	3 82¹⁷°	stable		insol	insol	sol dil min acids, and alk	
14	SnHPO₄	214 7	3 48¹⁵°	stable		insol		sol dil min acids	colorless, tabular
15	Sn(H₂PO₄)₂	312 8	3 17²²°	decomp	decomp		hydrolyzes		white, rhombic
16	Sn₂P₂O₇	411 5	4 00¹⁶°	stable		insol	insol	sol in conc min acids	amorphous, white
17	Sn(PO₃)₂	276 8	3 38²²°	hydroscopic		insol		sol diff conc min acids	glassy, amorphous
18	SnS	150 8	5 08¹⁵°	880	1230	0 000002	insol	sol conc	brown or gray needles
19	SnSO₄	214 8	6 18⁰°	SO₂,36°		18 9²⁰°	18 2¹⁰⁰°	HCl,(NH₄)₂Sₓ H₂SO₄	accicular, colorless
20	SnSe	197 9		86		insol	insol	sol conc	steel gray prisms
21	Sn₂Fe(CN)₆	449 3				insol	insol	sol hot conc HCl	white
22	Sn₃[Fe(CN)₆]₂	779 9				insol	insol	sol HCl	white

No.	Compound	Mol. wt.	Density	M.P.	B.P.	Sol. cold water	Sol. hot water	Sol. other reagents	Appearance
23	SnC_2O_4	206 7	3 56$^{18°}$		206 7	sl sol	decomp	sol oxalates	white
24	$SnBr_4$	438 4	3 35$^{85°}$	31	114 0	sol	decomp	alcohol, org liquids	colorless, rhombic
25	$SnCl_4$	260 5	2 28	—33		v sol	sol		liquid, white
26	$SnCl_4$ 2NH$_4$Cl	367 5	2 39			33 3$^{15°}$			octahedra
27	SnF_4	194 7	4 78	sublimes	340 0	v sol	decomp		white
28	SnI_4	628 4	4 70	143 5		v sol	decomp		orange red octahedra
29	SnO_2	150 7	6 90	1132		insol	insol		amorphous
30	SnO_2, natural	150 7	6 85			insol	insol		tetragonal or rhombic
31	K_2SnO_3 3H$_2$O	298 9	3 20			110 5$^{10°}$	sol		rhombic prisms
32	$Sn_2P_2O_7$ 10H$_2$O	623 6	3 98			insol	insol		white
33	Na_2SnO_3 3H$_2$O	266 7				61 3$^{20°}$	sol	insol HNO$_3$	rhombic
34	SnS_2	182 9	4 50	decomp		0 00002	insol	sol conc HCl, alk sulfides	yellow hexagonal
35	$Sn(SO_4)_2$ 2H$_2$O	346 7	4 85			v sol	v sol	sol dil H$_2$SO$_4$, HCl	rhombic leaflets
36	$SnSe_2$	277 1				insol	insol	insol dil acids, sol alkalies	gray
37	$SnTe$	246 2	6 48	780		insol	insol		gray crystals
38	$Sn(C_2H_3O_2)_4$ . .	236 7		182		sol	sol	sol acids	rhombic(?)
39	H_2SnO_3	168 7		decomp	decomp	s sol	s sol	sol dil acids, alkalies	amorphous
40	$H_{10}Sn_5O_{15}$ (meta)	843 6		decomp	decomp	insol	insol	insol acids, sol NaOH, KOH	amorphous, glass-like

Stannic sulfate may be formed by the solution of stannic hydroxide in dilute sulfuric acid, or by the action of oxidizing agents on stannous salts It forms oxy salts analogous to those of stannous sulfate, and a number of addition compounds (similar to the alums), of which potassium, rubidium, sodium, silver, calcium, strontium, barium, and lead compounds are best known Many double sulfates are formed with the rare metals

Tin carbonates are mentioned often in the literature, but they are not believed to exist If they do exist, they are exceedingly unstable, breaking down into the corresponding oxides An analogous situation exists in respect to the nitrates, which are not known in their pure forms but only as oxidized compounds which are generally tin oxides with adsorbed nitric acid Berzelius [72] states that stannic hydroxide dissolves copiously in nitric acid with a complete neutralization of the acid to form a solution which, if concentrated, deposits silky needles of stannic nitrate At 50° C it deposits almost all of its tin content as stannic oxide in the hydrated form This precipitate is soluble in ammonium nitrate When tin acts on metallic nitrates such as copper, the metal rapidly becomes colored with a mixture of precipitated copper and a basic salt When this salt is dried, it burns and at the same time gives off sparks When it is suddenly heated or struck, it explodes The salt is assumed to be a basic nitrate

Tin phosphates are produced by the addition of soluble phosphates to soluble tin salts The properties of a number of these are given in the table of solubilities Stannous hydrophosphate, the diphosphate, the meta and the pyrophosphate are all known, as well as analogous stannic salts

Addition compounds between the tin phosphates and alkaline-earth phosphates may be formed by fusion of these materials They are exceedingly complicated compounds and can be resolved upon analysis into phase rule systems of the oxides

COMPLEX TIN SALTS

Many complex tin salts found in the literature have not been thoroughly investigated, therefore comparatively little is known concerning them For completeness, some of the formulæ given by investigators are listed below. They include addition compounds, compounds forming as a result of the binary system of metals, and various complex salts

Bromostannites or double bromides are formed by the union of stannous bromides and the bromides of other metals They crystallize

[72] *Schweigger's J*, 6 284 (1812), *Ann chim phys* (2), 5 141 (1817)

out of solutions containing both these salts A number of double bromides found in the literature, with the formulæ given to them by the workers who studied them, are as follows

$SnBr_2 \ 2AlBr_3$	melting point 205° C
$SnBr_2 \ AlBr_3$	melting point 183° C
$SnBr_2 \ 2NH_4Br \ H_2O$	colorless needle-like crystals
$SnBr_2 \ 4NH_4Br \ H_2O$	crystals
$SnBr_2 \ 2NH_4Cl \ H_2O$	prismatic crystals, rhombic system
$SnBr_2 \ 2KBr \ H_2O$	, rhombic bipyramids
$Sn_3OBr_6 \ 12H_2O$	, colorless prismatic crystals

Various chlorides react with stannous chloride or with tin filings (as in the case of $SnCl_2 \ NH_4Cl \ H_2O$) to form chlorostannites A number of such compounds, other than those represented below, are supposed to exist, although little definite information is found in the literature Below are given a number which are known to have been somewhat studied

$SnCl_2 \ AlCl_3$	melting point 158 5° C
$SnCl_2 \ 2AlCl_3$	melting point 209 3° C
$SnCl_2 \ NH_4Cl \ H_2O$	, needle-like crystals, 57 374 grams soluble in 100 cc water between 16° and 81° C
$SnCl_2 \ BaCl_2 \ 4H_2O$	, prismatic crystals
$SnCl_2 \ HCl$	melting point $-27°$ C , crystals
$(N_2H_5)SnCl_3$	melting point 105° C , crystals, soluble in water, slightly soluble in alcohol
$SnCl_2 \ SnO \ 6H_2O$	insoluble in hot or cold water, soluble in dilute acids and alkalies
$SnCl_2 \ SrCl_2 \ 4H_2O$	needle-like crystals
$SnCl_2 \ TlCl$	melting point 244° C
$SnCl_2 \ 3TlCl$	melting point 310° C

Analogous to the bromides, the stannous iodide compounds appear in crystalline forms, most of them easily decomposed by water

NH_4SnI	greenish-yellow needles, decomposed by water
$SnIBr$	pale yellow needles
$SnICl$	. white needles
$SnClI$	yellow crystals, decomposed by water
$SnI_2 \ SnCl_4$	yellowish-red prisms
$2SnI_2 \ 2KI \ 9H_2O$	yellow silky needles, decomposed by water, soluble in hot alcohol
$SnI_2 \ RbI$	yellow needles
$2SnI_2 \ RbI$	orange-yellow cubic crystals
$NaSnI$	pale yellow crystals, decomposed by water

Brownish-red crystals of $Sn(HS)Cl$, easily decomposed by water, have been reported Two complex stannous sulfates known to exist are: $2Sn_3O_2 \ SO_4$, a red crystalline powder soluble in hot water; and $4K_2Sn(SO_4)_2 \ SnCl_2$ which appears as hexagonal prisms as a result of the action of warm potassium, sulfate solution on stannous chloride

The chlorobromides (in which one or two chlorine atoms are substituted for the corresponding bromine atoms), together with some of the numerous addition salts formed by stannic bromide and the bromides of other metals are given

$SnBr_4$ $2NH_4Br$	, specific gravity 3 505, pale yellow or colorless octahedral crystals, soluble in hot and cold water
$SnBr_4$ $CaBr_2$ $6H_2O$	slender needle-like crystals, deliquescent
$SnCl_3Br$	specific gravity 2 51 at 13° C, melting point — 31° C, boiling point 50° C at 30 mm pressure and 45° C at 20 mm pressure, colorless liquid
$SnBr_2Cl_2$	specific gravity 2 82 at 13° C, melting point — 20° C, boiling point 65° C at 30 mm pressure
$SnClBr_3$	specific gravity 3 12 at 13° C, liquid, melting point 1° C, boiling point 73° C
$SnBr_4$ $CoBr_2$ $10H_2O$	, yellowish-red tabular crystals, deliquescent
$SnBr_4$ $2HBr$ $8H_2O$	colorless prisms, or yellow needle-like crystals, ot triclinic plates
$SnBr_4$ $FeBr_2$ $6H_2O$	greenish-yellow granular crystals
$SnBr_4$ $2LiBr$ $6H_2O$	, yellow plates, hygroscopic
$SnBr_4$ $MgBr_2$ $10H_2O$	pale yellow tabular crystals
$SnBr_4$ $MnBr_2$ $6H_2O$	pale yellow crystals, deliquescent
$SnBr_4$ $NiBr_2$ $8H_2O$	, apple-green granular crystals, deliquescent
$Sn_2O_2Br_4$ $10H_2O$	colorless needle-like crystals
$SnBr_4$ $2KBr$	specific gravity 3 783, octahedral crystals, stable in air, easily soluble in water
$SnBr_4$ $2NaBr$ $6H_2O$	pale yellow prismatic or acicular crystals, monoclinic system
$SnBr_4$ $SrBr_2$ $6H_2O$	pale yellow crystalline mass, deliquescent

The literature offers formulæ for stannic oxychlorides and chlorostannates These, with their crystal forms, are

$SnCl_4$ $2NH_3$	yellowish-white acicular crystals, soluble in cold water
$SnCl_4$ $BeCl_2$ $8H_2O$	white powder
$SnCl_4$ $CaCl_2$ $6H_2O$	rhombohedral crystals
$SnCl_4$ $2CsCl$	specific gravity 3 3308 at 20 5° C, octahedral and cubic crystals, insoluble in hydrochloric acid, decomposed by sulfuric and hydrofluosilicic acids
$Sn(N_2H_4)_2Cl_2$	decomposed by water, insoluble in aqueous ammonia
$SnCl_4$ $CoCl_2$ $6H_2O$	specific gravity 2 699, rhombohedral crystals, trigonal system
$SnCl_4$ $2HCl$ $6H_2O$	melting point 20° C, tabular crystals
$SnCl_4$ $2LiCl$ $8H_2O$	colorless octahedral crystals, soluble in water
$SnCl_4$ $MgCl_2$ $6H_2O$	specific gravity 2 08, rhombohedral crystals, deliquescent, soluble in hot and cold water
$SnCl_4$ $MnCl_2$ $6H_2O$	specific gravity 2 215, pale red rhombohedral crystals, trigonal system, deliquescent
$SnCl_4$ $NiCl_2$ $6H_2O$	specific gravity 2 699, greenish rhombohedral crystals, trigonal system
$SnCl_4$ N_2O_3	, lemon-yellow crystalline mass
$SnCl_4$ $2RbCl$	octahedral crystals
$SnCl_4$ $2NaCl$ $6H_2O$	, crystals
$SnCl_4$ $SrCl_2$ $6H_2O$	prismatic crystals
$SnCl_4$ $ZnCl_2$ $6H_2O$	crystals

SnCl₄ 2NOCl	specific gravity 2 60, melting point 180° C, pale yellow octahedral crystals, decomposed by water
SnOCl₂	soluble in water
Sn₃O₄Cl₂ 4H₂O	soluble in small amount of water, soluble in alcohol, translucent deliquescent mass
(SnO)₄Cl₇ 5H₂O	yellow plates, soluble in water and alcohol
SnCl₄ 2KCl	specific gravity 2 70, octahedral crystals, soluble in hot and cold water
SnCl₄ POCl₃	crystals, melting point 58° C, boiling point 180° C
SnCl₄ PCl₅	colorless crystals, decomposed by water
SnCl₄ 5H₂S	white crystals
SnCl₄ 2SCl₄	melting point 37° C, yellow crystals, soluble dilute nitric acid, chloroform, carbon bisulfide, phosphoryl chloride, benzene, ether, acetic ether, sulfur chloride

Stannic fluoride unites with other metallic fluorides, forming fluo-stannates with formulæ and crystal shapes as follows

SnF₄ 2NH₄F	trigonal crystals
SnF₄ BaF₂	monoclinic crystals, solubility in 100 cc of water is 5 6 grams, at 18° C
SnF₄ CaF₂ 2H₂O	monoclinic crystals
SnF₄ CdF₂ 6H₂O	trigonal crystals
SnF₄ 2CsF	hexagonal plates
SnF₄ CuF₂ 4H₂O	blue monoclinic crystals
SnF₄ PbF₂ 3H₂O	monoclinic prisms
SnF₄ 2LiF 2H₂O	monoclinic prisms
SnF₄ MgF₂ 6H₂O	trigonal crystals
SnF₄ MnF₂ 6H₂O	trigonal crystals
SnF₄ NiF₂ 6H₂O	trigonal crystals
SnF₄ 2KF H₂O	specific gravity 3 053, white crystals, slightly soluble in water
SnF₄ 3KF HF	monoclinic prisms
SnF₄ 2RbF	hexagonal plates
SnF₄ 2NaF	crystalline crust, solubility in water at 20° C is 5 5 grams
SnF₄ SrF₂ 2H₂O	monoclinic crystals, solubility in water at 18° C is 18 2 grams
SnF₄ ZnF₂ 6H₂O	specific gravity 2 445, crystals

Replacement compounds of stannic iodide in which chlorine or bromine replaces some of the iodine are

SnBr₂I₂	specific gravity 3 631 at 15° C, orange-red crystals, melting point 50° C, boiling point 225° C or 130° C in vacuo, soluble in cold water, solution decomposing at 80° C
SnBr₃I	yellowish-red crystals
SnCl₂I₂	specific gravity 3 287 at 15° C, red liquid, boiling point 297° C, although it begins to distill at 190° C, soluble in water, benzene, chloroform, carbon bisulfide
SnS₂I₄	red rhombic crystals, decomposed by water, hydrochloric acid, nitric acid, aqua regia

In addition to the stannates given in the table, those listed below are of interest, but many of their physical and chemical properties are not as yet thoroughly confirmed

$SnO_2 (NH_4)_2 CuO 2H_2O$	slightly soluble in cold water, soluble in acids
$BaSnO_3 7H_2O$	slightly soluble in cold water, soluble in nitric acid
$CaSnO_3$	needle-like crystals
$CaSnO_3 3H_2O$	insoluble in water, soluble in nitric acid
$CoSnO_3 6H_2O$	rose-red crystals
$CuSnO_3 4H_2O$	pale blue crystals, soluble in aqueous ammonia
$Hg_2SnO_3 5H_2O$	.yellow precipitate, turning green
$HgSnO_3 6H_2O$	white, turning dark green
$NiSnO_3 5H_2O$	pale green cubic crystals
$KSnO_4 2H_2O$	white amorphous powder
$K_2Sn_3O_{11} 4H_2O$	.horny translucent colloid, soluble in water
$Ag_2SnO_3 2H_2O$	dark red precipitate, soluble in dilute nitric acid, insoluble in ammonia
$Ag_2Sn_3O_{11}$	grayish powder turning deep red, soluble in dilute nitric acid, insoluble in ammonia
$Na_2SnO_3 10H_2O$	long prismatic crystals
$Na_2Sn_3O_{11} 8H_2O$	crystalline powder, slightly soluble in water
$Na_2Sn_3O_{10} 8H_2O$	.insoluble in alcohol and sodium hydroxide
$NaSnO_4 2H_2O$	white amorphous powder, slightly soluble in cold water, decomposed by hot water
$SrSnO_3 3H_2O$	white crystalline powder
$ZnSnO_3 2H_2O$	colorless crystals, soluble in dilute acids

Crystal forms of some of the salts of tin and phosphorus are recorded They are·

Sn_4P_3	specific gravity 5 18
$Sn_2O(PO_4)_2$	octahedral crystals
SnP_2O_7	cubic crystals
$Na_3Sn(PO_4)_2$	tetragonal prisms
$NaSn_2(PO_4)_2$	rhombohedral crystals

The complex sulfides and sulfates of tin, according to various investigators, formed by the reaction between stannic salts and sulfuric acid or the sulfides or sulfates of other metals are given below Their study is quite complicated

H_2SnS_3	gray prisms, insoluble in hot or cold water
$(NH_4)_2SnS_3 3H_2O$	thin yellow plates
$BaSnS_3 8H_2O$	lemon-yellow crystals, soluble in cold water
$Ca_2SnS_4 14H_2O$	lemon-yellow crystals, very soluble in water
$PbSnS_3$	specific gravity 6 36, grayish-black rhombic crystals, decomposed by hot hydrochloric or nitric acid
$Sn_2S_3O 11\frac{1}{2}H_2O$	slightly soluble in water, soluble in ammonium carbonate
$K_2SnS_3 3H_2O$	.colorless transparent prisms, sparingly soluble in water
$K_4SnS_4 12H_2O$	monoclinic prisms
$Na_2SnS_3 2H_2O$	yellow octahedral crystals, melting point at temperature approaching redness
$Na_4SnS_4 12H_2O$	colorless monoclinic crystals
$SrSnS_3 12H_2O$	thick colorless prisms
$Bi(OH)Sn(SO_4)_3$	rhombic leaflets
$CaSn(SO_4)_3 3H_2O$	colorless cubes
$CeHSn(SO_4)_4$	colorless microcrystalline powder
$LaHSn(SO_4)_4$	small six-sided plates
$Sn(OH)_2SO_4$	white needles, soluble in cold water

K$_2$Sn(SO$_4$)$_3$	needle-like crystals
Rb$_2$Sn(SO$_4$)$_3$	six-sided leaflets
Ag$_2$Sn(SO$_4$)$_3$ 3H$_2$O	needles
Y$_2$Sn(SO$_4$)$_6$	microcrystalline powder

Tin Salts in Commerce

The only tin salts which are of commercial importance or are consumed in large quantities are the dioxide, the stannic, and stannous chlorides, the stannous sulfate, stannous tartrate, phosphate, and oxalate

Stannic oxide is known under the commercial names of tin oxide, tin dioxide, tin peroxide, or flowers of tin It is made commercially by heating molten tin in the air or in large furnaces through which air is blown over the surface of the molten metal, or into which air is bubbled under pressure through the molten metal The raw material is usually Straits tin or equivalent quality The furnaces are often equipped with dust collectors, usually of the bag-house type, for catching the very fine oxide particles After manufacture, the material is screened, in some cases ground, and separated into grades The commercial containers are usually wooden kegs The grades of the product are the white or pure, and the technical grade gray The oxide finds extensive use in the glass industry for the production of opaque glasses, in ceramic manufacture, the making of porcelain and enamels on metal, particularly cast iron, examples of which are found in our bathtubs and white enameled sinks and sanitary ware Other uses are in connection with putty making, polishing powders, special abrasives, and electrical uses It also finds some application in textile manufacture

Because of its relatively high price, stannic oxide is finding increasing competition from antimony oxide which has replaced it in some of its applications, either in part or wholly

Stannic chloride in its anhydrous form is produced to the greater extent as the result of the recovery of tin from tin plate scrap by the chlorine process This material is the anhydrous product and is a colorless, thin, fuming, caustic liquid which moisture or water converts into a buttery, crystalline substance known as butter of tin The anhydrous stannic chloride must be kept hermetically sealed for stability It is also made commercially by dissolving granulated tin in concentrated hydrochloric acid of 20° Baumé It is soluble in a large number of organic solvents such as alcohol, ether, carbon bisulfide, oil of turpentine, and to some extent in benzol The grades are water white and technical It is sold either in the anhydrous liquid form or as crystals, SnCl$_4$ 5H$_2$O, or as solutions of various concentrations The

containers for the anhydrous form are iron drums or glass bottles,
glass containers are used for the other grades The material is used
extensively in dyeing and in silk weighting, often as the pentahydrate
or as pink salt, which is ammonium-stannic chloride, $(NH_4)_2SnCl_6$
Its use as a mordant in dyeing depends on the ready decomposition of
the salt and its hydrolysis to stannic hydroxide from weak solutions
of the chloride The stannic hydroxide resulting is adsorbed on the fiber
With the help of this salt, a permanent red is obtained from cochineal
Its use in the weighting of silk consumes the greater part of the pro-
duction Stannic chloride is also used in the manufactuie of fuchsine
It is commercially known as tin chloride, butter of tin, tin tetrachloride,
often erroneously as tin bichloride, and tin oxymuriate

   Stannous chloride, known commercially as tin bichloride or tin salt,
is made by treating tin with a calculated quantity of hydrochloric acid
The crystalline form, $SnCl_2$ $2H_2O$, is the result of crystallization out
of solution In the anhydrous form it is a heavy, colorless, corrosive
liquid, giving off fumes on exposure to the air The hydrated form is a
white crystalline solid and is not classed as a dangerous article under
the Interstate Commerce Commission regulations The salt is largely
used in dyeing, in the manufacture of textiles, and in calico printing
as a mordant It also finds some application in glass making, ceramics,
ink making, tin plating, and tin coatings, to a small extent in sugar
bleaching, in fermentology, and in a large variety of applications of
tin salts The major use is in textile dyeing and calico printing, as a
mordant Its commercial forms are the anhydrous, the crystalline, and
solutions of various concentrations

   Stannous sulfate is commercially obtained either by the action of
sulfuric acid on stannous chloride with the production of a ponderous
white or yellowish powder or crystals, or else by the action of sulfuric
acid, often in the presence of chlorides, on tin There is only one com-
mercial grade made, and that is the technical variety The containers
are wooden kegs The salt is used in the dyeing industry and to a small
extent in electroplating Stannous sulfate employed in refining baths
in tin electrometallurgy is manufactured by the consumer

   Stannous oxalate finds application in the dyeing and textile-printing
industries It is a white ponderous crystalline powder obtained by the
action of oxalic acid on stannous oxide, or on stannous chloride It is
soluble in acids The only commercial grade is the technical one, and
the containers are wooden kegs

   Stannous tartrate has characteristics quite similar to those of stan-
nous oxalate, and is obtained by the action of tartaric acid on stannous

chloride The technical grade is soluble in water The containers are wooden kegs, and the material finds application in calico printing and in textile dyeing A similar situation holds for stannous phosphate produced by the action of phosphates on stannous chloride

CHAPTER 14

CORROSION

THE EFFECT OF WATER

Tin is widely used in alloys, in the manufacture of tin foil, and for coating other metals, such as copper and iron, to render them more resistant to corrosion Tin metal itself is very resistant to corrosion by the atmosphere or the various gases contained therein as a result of manufacturing processes Water affects tin hardly at all At ordinary temperatures there is no tendency toward oxidation Were it not for the fact that tin is electronegative to iron and strongly accelerates its corrosion in the presence of atmospheric electrolytes if the two metals be exposed at the same time,—that is, if the coating be non-continuous, —tin would serve admirably as a protection to sheet steel or iron This statement needs modification, inasmuch as the relative electrode potentials of tin and iron depend upon the corroding agent, and in some cases tin is electropositive to iron As has been pointed out under tin compounds, the metal dissolves rather slowly in most acids, but reacts readily with nitric acid to form metastannic acid Tin also reacts with water solutions of the alkalies to form soluble stannites and stannates The corrosion of tin in the form of tin plate in one of its widest uses, that of tin cans, has been discussed in a separate chapter

Small amounts of tin, when added to other metals or alloys, markedly increase their corrosion resistance This point has been discussed in connection with bronzes and the copper-tin alloys Desch and Whyte [1] in their studies of the microchemistry of corrosion, show the protective influence of tin on the copper-zinc alloys

Even the purest water has practically no solvent action upon pure tin Long experience has shown that block-tin pipe, when the tin metal of which it is made is of good quality, is one of the best materials for conveying distilled water to be used for experimental purposes Carbonated water has practically no solvent effect on tin metal When the solubility of metals in water is determined by the conductivity method, it is found that twice distilled water has practically no solvent

[1] *Metal Ind* (*London*), 11 430 432 (1914), 12 115 117 (1914), *J Inst Metals*, 10 304 (1913)

effect on tin when the resultant effect is tested for by delicate conductivity measurements

THE CORROSIVE ACTION OF HALIDES

The halides are among the most active substances corroding tin The effect of a material known under the name of Flammon, which consists of a mixture of ammonium fluoride and hydrofluoric acid, on the metals used in the brewing and related industries has been investigated by Will and Landtblom [2] All percentages of Flammon show no effect on tin metal

Hale and Foster,[3] in their study of the action of dilute solutions of acids, alkalies, and salts upon metals, found that tin is appreciably attacked by calcium-chloride solutions of fifth normal concentrations, although only aluminum and nickel are attacked less, while zinc, cast and wrought iron, lead, and copper are more readily attacked Their results are of the weight-loss type, and at the present time, in view of our better corrosion technique, are of little value except as indications The attack on tin was about one and one-half times greater than that on nickel, but only about one-third of that on lead

Solutions of ferric chloride, as a result of their acidic reaction, markedly affect tin Together with small amounts of tin chlorides and a little hydrochloric acid, ferric chloride has been patented for the recovery of tin from tin-plated sheets, but to date it has found practically no industrial application

The attack of tin by magnesium-chloride solutions occurs to some extent, but the action is slow, being of the same order as the attack by calcium chloride The resistance, however, of metals to magnesium chloride, as studied by Hale and Foster,[4] shows that only nickel is superior in its resistance to the attack by this salt Halla [5] studied the susceptibility of tin plate to attack by neutral magnesium-chloride solutions He found that when the partial pressure of oxygen is high, the corrosion of tin plate in gas meters is accelerated When, however, the partial pressure of oxygen is lowered by the presence of illuminating gas, the salt seems to retard solution of oxygen in the liquid, and at the same time decreases the corrosion rate

Hale and Foster [6] state that sodium chloride by itself in fifth normal concentrations does not corrode tin The results of other workers, however, seem to indicate that this salt has an appreciable corrosion

[2] *Z ges Brauw*, **42** 81 82 (1919)
[3] *J Soc Chem Ind*, **34** 464 (1915)
[4] *Loc cit*
[5] *J Gasbel*, **56** 908 (1913), *Chem Zentr*, **II** 1709 (1913)
[6] *Loc cit*

effect on the metal Jermstad and Gaule [7] report that when tin test pieces are boiled in a 1 per cent salt solution and are not in rubbing contact, no tin is dissolved If the test pieces be in rubbing contact, colloidal solution of the tin takes place Fink and Mantell [8] have shown that the addition of sodium chloride to dilute solutions of sulfuric acid markedly increases the rate of solution of the tin by the acid Jarvinen [9] studied the attack of tin by sodium-chloride solutions

When an outside electromotive force is impressed on a cell in which tin is the anode in a sodium-chloride solution, the metal dissolves at a relatively slow rate

Stannous chloride readily attacks tin metal It has often been suggested in connection with acids and other salts as a detinning material for the removal of tin from tin-plate scrap It accelerates corrosion of tin by mineral acids Stannous chloride attacks the metal most readily at the grain boundaries It has been used as an etching reagent in the microscopic study of tin and its alloys

As early as 1850, Wohler [10] studied the action of sulfur chloride on tin He found that the action was very marked, inasmuch as tin reacted readily with this compound His results agree with those of Nicolardot,[11] who found that of all the metals only tin, aluminum, mercury, and iron react with sulfur chloride In 1916 Domanicki,[12] after reviewing all previous work on this reaction, found that ether accelerates the combination as a result of the formation of a complex between the ether and the sulfur chloride

Thionyl chloride reacts with most of the common metals and metalloids North and Hageman [13] state that when tin is heated in a sealed tube with thionyl chloride to 150° to 200° C, reaction takes place with the formation of stannous chloride, sulfur dioxide, and sulfur chloride In the presence of an excess of thionyl chloride, the stannous salt is oxidized to the stannic form At lower temperatures, thionyl chloride has an appreciable action on tin metal

The halides in their free form unite directly with tin, forming stannic salts Fluorine does not react readily with tin at low temperatures, but at 100° C it forms stannic fluoride Dried chlorine and bromine act on tin at ordinary temperatures Liquid chlorine markedly attacks tin The attack of chlorine on tin at room temperatures was utilized in the chlorine process of detinning described elsewhere in this

[7] *Schweiz Apoth Ztg*, 57 89 92, 109 113 (1919)
[8] *Eng Mining J* 125 452 455 (1928)
[9] *Z Untersuch Nahr Genuss*, 50 221 (1925)
[10] *Ann.*, 73 375 (1850).
[11] *Compt rend*, 147 1304 (1908)
[12] *J Chem Soc*, 112, II 369 (1917)
[13] *J Am Chem Soc*, 34 890 (1912)

volume Even in low concentrations, when mixed with other gases, the free halogens markedly attack the metal Tin is readily susceptible to attack by iodine, whether in the form of solution or vapor The rate of solution of tin is abnormally high, as shown by the work of Van Name and Bosworth [14] in their study of the attack of various metals by a solution of iodine in potassium iodide Iodine vapors, even in low concentrations, rapidly tarnish tin metal and tin coatings Tammann [15] showed that tin was soon colored yellow when placed in the desiccator in an atmosphere of iodine vapor, and that a fine, dark dust gathered on the surface of the metal

THE EFFECT OF ACIDS ON THE CORROSION OF TIN

All of the halogen acids attack tin According to Berthelot, in agreement with the thermal values of the reaction, tin is easily attacked by hydrogen iodide and hydrogen bromide, less readily by hydrogen chloride, and but feebly by hydrogen fluoride It is slowly dissolved by dilute hydrochloric acid, and with hot concentrated hydrochloric acid, hydrogen is evolved and stannous chloride is formed The dissolution of the tin is accelerated by the presence of a little platinic chloride or if the tin be in contact with copper, silver, lead, antimony, platinum, or other of the noble metals Nollner [16] states that the action of hydrochloric acid on tin ceases when the solution contains one mol of stannous chloride for every two mols of hydrochloric acid Watts and Whipple [17] found that with normal hydrochloric acid 0 0016 and 0 0015 gram per sq cm were dissolved from hammered and cast tin respectively at 38° C in 20 hours When potassium permanganate to the extent of about 5 per cent was present in solution, approximately 0 06 gram per sq cm was dissolved from cast tin The rate of corrosion of cast tin in normal hydrochloric acid is fairly low, and that of hammered tin is about 20 per cent greater Since tin dissolves in hydrochloric acid with the evolution of hydrogen, the addition of potassium permanganate, a strong oxidizing agent, rapidly accelerates the corrosion Hale and Foster [18] found that fifth normal hydrochloric acid dissolved tin at the rate of 0 42 gram per sq dcm per day during seven days at 20° C, and 0 90 gram during 28 days The resistance of tin among the metals tested is exceeded only by that of nickel and aluminum, but tin was found to be considerably better than zinc, cast and wrought iron, lead, and copper The superior corrosion resistance of aluminum was due to the

[14] *Am J Sci*, 32 207 (1912)
[15] *Z anorg allgem Chem*, 111 78 89 (1921)
[16] *Liebig's Ann*, 115 233 (1860)
[17] *Trans Am Electrochem Soc* 32 257-284 (1917)
[18] *J Soc Chem Ind*, 34 464 (1915)

formation of the protective layer of oxide Whitman and Russell [19]
found that the corrosion of tin by hydrochloric acid is increased by
the presence of oxygen Salkowsky [20] states that if hydrogen dioxide be
present, free chlorine is evolved and the tin is attacked more readily
Prins [21] found that the presence of easily reducible substances like
benzaldehyde or nitrobenzene accelerates the attack of acids on tin
Vaubel [22] states that during the dissolution of polished tin in hydro-
chloric acid, a black powder is deposited This dissolves only very slowly
even in concentrated acid He suggests that this may be a peculiar
modification of the metal produced by the reduction of stannous chlo-
ride by nascent hydrogen

The rapid attack of tin by the halogen acids and halide salts is well
known Alloys containing tin, antimony, and lead are readily dissolved
by a strong solution of hydrochloric acid containing a little nitric acid

Hot hydrobromic or hydroiodic acid readily dissolves tin When
mixtures of hydrochloric and nitric acids act on tin, ammonia and
hydroxylamine are formed

Chloric acid readily attacks tin, causing it to pass in solution with
the formation of stannic chloride, without the evolution of hydrogen
and with the production of only very small amounts of stannic acid

Hypochlorous acid attacks tin, and the action is accelerated by in-
creasing concentrations of the acid or by the presence of other acids,
particularly chloric acid

Pure liquid hydrocyanic acid has no action on pure tin, and prob-
ably none on commercial tin Gray and Hulburt [28] state that the contact
of this acid with commercial tin causes the decomposition of the acid,
and that the use of tin in connection with hydrocyanic acid should be
avoided Taplay [24] states that hydrocyanic-acid gas plays a part in the
corrosion of tinned sheet-iron parts of gas meters employed in con-
nection with the distribution of manufactured gas

Nitric acid readily reacts with tin and exerts a strong corrosion
effect The oxides of nitrogen in small concentrations tarnish tin metal
Nitric acid oxidizes considerably more tin than it dissolves, and hot
nitric acid converts the metal completely to hydrated stannic oxide The
products of the action of nitric acid on tin vary greatly with the
concentration of the acid and with the temperature Hale and Foster [25]
found that with fifth normal nitric acid, the loss of metal per sq dcm

[19] *J Ind Eng Chem*, 17 348 (1925), *Munch med Wochschr*, 72 1161 (1925)
[20] *Chem Ztg*, 40 448 (1916)
[21] *Proc Acad Amsterdam*, 23 1449 (1922)
[22] *Ber*, 57, B 515 (1924)
[23] *Calif Agr Expt Sta*, *Bull*, 308 408 428 (1919)
[24] *Gas J*, 150 583 587 (1920), *Gas World*, 72 481 485 (1920)
[25] *Loc cit.*

at 20° C was four grams per day in 7 days, and 7 2 grams per day in 28 days Aluminum and copper are markedly superior in their corrosion resistance to nitric acid The presence of nitric acid in hydrochloric acid markedly accelerates the corrosion by hydrochloric acid

Barth [26] has studied the loss of weight of cobalt-tin, copper-tin-cobalt, and copper-tin-molybdenum alloys in various concentrations of nitric acid

Tin is appreciably attacked by sulfuric acid, even in dilute solutions The corrosion is accelerated by the presence of chlorides In one of the early articles on the corrosion of tin by sulfuric acid, Muir and Robbs [27] studied the effect of the concentration of the acid and the relative proportions of hydrogen, hydrogen sulfide, sulfur dioxide, and sulfur produced They found that when the molar proportions of sulfuric acid and water are as seven to two at 20° to 25° C , there is but little action No hydrogen sulfide is produced, but little sulfur, and a trace of sulfur dioxide is formed At 110° to 120°, small amounts of hydrogen sulfide and appreciable quantities of sulfur and sulfur dioxide are produced When the acid-water concentrations are equal at 20° to 25° C , traces of hydrogen sulfide and sulfur are found At 110° to 120° C a little hydrogen and sulfur, some hydrogen sulfide, and a large quantity of sulfur dioxide are formed When the acid-water proportions are as one to three, there is only a slow action at 20° to 25° , but at 110° to 120° much hydrogen sulfide and a trace of sulfur dioxide are formed When the acid-water concentrations are as one to five, at 25° C the action is very slow , at 110° to 120° C hydrogen and a trace of hydrogen sulfide are given off Watts and Whipple [28] made a careful study of the corrosion of tin in normal sulfuric acid They found that 0 0006 gram per sq cm of tin was dissolved in 20 hours at 38° C The addition of sodium chlorate caused an enormous acceleration of the corrosion With approximately 5 per cent of sodium chlorate, 0 13 gram of tin per sq cm was dissolved in 20 hours at 38° C Rather unexpectedly, potassium dichromate was found to reduce the corrosion figure in grams per sq cm from 0 0006 to 0 0003 Instead of strongly accelerating the corrosion, it reduced it to less than half This effect was the result of the formation of a fine white precipitate which acted as a protective coating Hale and Foster [29] found that with fifth normal sulfuric acid at 20°, 0 022 gram per sq dcm per day was lost during 7 days, and 0 25 gram per sq dcm per day during 28 days

[26] *Metallurgie,* 9 261 (1912)
[27] *Chem News* 45 69 (1882)
[28] *Trans Am Electrochem Soc ,* 32 257 284 (1917)
[29] *Loc cit*

Oxygen accelerates the attack of tin by sulfuric acid In dissolving tin, when sulfate electrolytic refining baths are made, it is found that the tin dissolves much more rapidly in the electrolyte if baskets containing the metal be exposed alternately to the solution and to the air Hydrogen dioxide does not affect the rate of dissolution of tin by sulfuric acid Pyrosulfuric acid dissolves tin with the evolution of heat, forming stannous sulfate and sulfur oxides

Formaldehyde has little effect in decreasing the corrosion of tin by sulfuric acid Van Name and Hill [30] and Selvig and Enos [31] studied the rate of solution of tin in sulfuric acid and in mine waters containing sulfuric acid and iron and aluminum sulfates

Jones [32] states that tin metal stands oleum very well and is useful for making condensing coils where copper would be attacked The advisability of the use of tin in this connection is questionable, inasmuch as it can be supplanted by cheaper metals which have sufficient corrosion resistance

Tin is corroded somewhat by various concentrations of chromic acid, as has been shown by Van Name and Hill [33] When the acidity is sufficiently high, the determining factor of corrosion is diffusion

A large number of patents have been taken out for etching agents, employing the numerous salts of boric, acetic, tartaric, and nitric acids which are to be used in dilute acid solutions for commercial etching The salts are to be used either singly or in combination with each other Although these salts themselves do not readily corrode tin metal, it is probable that they have some influence on the rate of corrosion The attack of these etching agents is usually more severe along the grain boundaries of the metal surface than in the interior of the grain

A number of tests to determine the effect of the attack of acetic acid on block tin are reported by Calcott and Whetzel [34] Their corrosion figures are given in Table 17

Block tin was subjected to the attack of 20, 60, and 100 per cent acetic acid at 25° C and at the boiling point of the solutions Although the data were obtained by one of the early corrosion methods, they clearly indicate that acetic acid may be safely handled in tin, at least up to 60 per cent concentration It is very likely possible that at room temperatures somewhat higher concentrations may be stored in tin or tin-lined containers The results also show that boiling acetic acid should not be handled in tin in concentrations much over 20 per cent

[30] *Am J Sci*, 42 301-332 (1916)
[31] *Carnegie Inst Tech Cooperative Mining Courses Bull*, 4 (1922)
[32] *Chem Age*, 4 394 395, 416 417 (1921)
[33] *Loc cit*
[34] *Trans Am Inst Chem Eng*, June, 1923

TABLE 17

CORROSION OF TIN BY VARIOUS ACIDS

Acid	Description or Concentration, Per Cent		Temp ° C	Rate of Corrosion, Inches Penetration per Month
Acetic	20		25	0 000412
			B P	0 000896
	60		25	0 000511
			B P	0 00131
	100		25	0 00160
				0 0140
	Acid	Anhydride		
Acetic + anhydride	10	90	25	0 00169
			B P	0 0103
	60	40	25	0.00140
			B P	0 0456
	80	20	25	0 00405
			B P	0 0588

A number of organic fruit acids, such as citric and malic, attack tin quite rapidly in contact with air, but scarcely at all when air is excluded At any rate, the attack is very much lessened at reduced oxygen pressures A similar condition holds true for lactic acid, which attacks tin in the presence of oxygen but scarcely at all in vacuo or in an atmosphere of carbon dioxide Appreciable concentrations of lactic acid definitely corrode tin

Since tin is widely used in coating steel plate for use in containers for canned foods, a great deal of attention has been given to its corrodability by organic acids The corrosion of tin plate by food products is discussed separately in another chapter As has been pointed out under malic and lactic acids, the effect of the dilute fruit and vegetable acids on tin is very small in the absence of air, but the attack is accelerated by oxidizing agents, particularly nitrates

Oxalic and tartaric acids dissolve tin in the presence of air, but the removal of oxygen definitely retards the action

The presence of pectin substances, particularly in canned tomatoes, materially retards corrosion of tin coatings

Phenol tarnishes and corrodes tin When practically pure phenol is boiled with tin, it becomes opalescent The phenol vapors are accompanied by benzol, which is a reduction product This reaction has been studied by Zoller [35] As a result of the reaction, tin is oxidized The reaction does not seem to take place to any appreciable extent at room temperatures, but only above 100° C

Picric acid shows a definite corrosion effect on tin Similar to other

[35] *J Am Chem Soc*, **43** 211 (1921)

organic reducible compounds, the acid shows a strong accelerating effect upon the corrosion of tin in sodium hydroxide According to Watts and Whipple,[36] amalgamation does not protect the tin, since no hydrogen is evolved

The moist vapors of salicylic acid, according to Whittaker,[37] do not seem to affect tin when the metal is used as a condensing surface When the vapors of salicylic acid are condensed in iron equipment, they are given a violet coloration, but there is no coloration effect when condensed in tin equipment

THE CORROSIVE EFFECT OF ALKALIES

When present in small amounts in manufactured gas, gaseous ammonia has been considered to cause corrosion of gas mains and the tinned sheet iron parts of gas meters Taplay [38] has attributed the corrosion to the products resulting from the reactions between carbon bisulfide and ammonia Henderson and Galletly [39] state that when tin is heated in ammonia gas, the surface of the metal becomes frosted and blistered At high temperatures the ammonia is decomposed The metal seems to "fix" no appreciable amount of nitrogen If the work of Henderson and Galletly be confirmed, it is probable that the corrosion of gas meters may be due to contact between the ammonia and the iron at imperfections of the tin coating Liquid ammonia, according to Kraus,[40] does not dissolve tin, but when metallic sodium has been first dissolved in the ammonia, the liquid has a strong solvent action on tin metal Kraus states that solutions of tin in this reagent are red, and readily conduct the electric current Hale and Foster,[41] in their corrosion tests on tin acted on by ammonium hydroxide, indicate that this reagent is without attack on tin metal

Tin is readily attacked by sodium and potassium hydroxides The corrosion in potassium hydroxide has been studied by Nutton and Law [42] with the object of determining the potential of hydrogen liberated from this metal, and the possible application of electrolytic reduction to organic processes Hale and Foster show that tin is appreciably soluble in caustic soda, giving a weight loss of 0 30 gram per sq dcm per day for 7 days, and 0 50 gram per sq dcm per day for 28 days, being markedly inferior to all the other metals tested, and being better only than aluminum and lead Tin corrodes slowly in pure sodium-hydroxide

[36] *Trans Am Electrochem Soc*, 32·257 (1917)
[37] *Trans Am Inst Chem Eng*, June, 1923
[38] *Gas J*, 150 583 (1920), *Gas World*, 72 481 (1920)
[39] *J Soc Chem Ind*, 27 387 (1908)
[40] *J Am Chem Soc*, 29 1556 (1907)
[41] *J Soc Chem Ind*, 34 464 (1915)
[42] *Trans Faraday Soc*, 3 part I, 50 (1907)

solution Oxidizing agents, such as potassium permanganate or picric acid, markedly intensify the attack Sodium arsenate and potassium nitrate do not accelerate the corrosion

In practice, tin is found to dissolve anodically in the tetravalent form, giving stannate as follows

$$Sn + 4\oplus - Sn''''$$
$$Sn'''' + 6OH' - SnO_3'' + 3H_2O$$
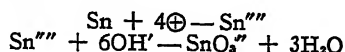
This, together with the fact that alkaline stannite solutions decompose spontaneously to give metallic tin and stannate, leads to the belief that the relation between stannic and stannous ions and tin metal was similar to that between cupric and cuprous ions and metallic copper Opposed to this was the fact that tin dissolves anodically in acid solutions as stannous ions Goldschmidt and Eckardt [43] found that although pure tin readily became passive, it also readily dissolved in alkaline solutions to form stannous ions Foerster and Dolch [44] found that tin is not really analogous to copper in this connection, but that tin metal-stannous ion and not tin metal-stannic ion is the stable system Anodic tin readily passivates in alkaline solution as the result of the formation at definite concentrations of colloidal tin compounds which are precipitated on the electrode This prevents a diffusion of the stannous ions, and the anode potential is raised to the value necessary for oxygen evolution The oxygen rapidly oxidizes the stannite ion to stannate Any insoluble impurities present in the tin favor the occurrence of this film action The higher the temperature and the lower the current density, the more tin can be dissolved before the formation of stannate occurs Eventually the surface becomes coated with stannic compounds, and the tin becomes passive

Tin metal is thus seen to be readily corroded by alkalies, but the corrosion may be slowed down as the result of the formation of oxide coatings by the chemical action of the hydroxides on the tin metal

THE EFFECT OF SOLUTIONS OF THE SALTS OF THE INORGANIC ACIDS

Salt solutions act more rapidly on tin metal than does water In certain cases, as for example the chlorides which have been previously discussed, the corrosion is quite marked Salts which are decidedly alkaline, such as the carbonates and bicarbonates, corrode tin in a manner quite similar to the action of hydroxides

Salt solutions, such as warm aqueous solutions of ammonium chlo-

[43] *Z phys Chem*, 56 385 (1906)
[44] *Z Elektrochem*, 16 599 (1910)

ride, sodium chloride, potassium hydrosulfate, potassium aluminum sulfate, and many other soluble sulfates and chlorides dissolve tin

The action of 10 per cent ammonium persulfate in sulfuric-acid solution causes marked corrosion Ammonium sulfate, ammonium sulfocyanide, and ammonium thiosulfate all corrode tin The action of calcium hypochlorite on tin is somewhat analogous to the action of hypochlorous acid White [45] states that when calcium hypochlorite is in contact with tin, oxygen is liberated, and that the hypochlorite slowly oxidizes tin to stannic oxide with the evolution of chlorine There are a number of references in the literature concerning the action of alkali hypochlorites on tin They all agree that there is appreciable destruction of the metal surface. Weston [46] has investigated the effect of small amounts of calcium hypochlorite in water upon tin and other metals In dilute solutions, the action is relatively slow

Taplay,[47] as a result of his investigation of the corrosion effect of ferric sulfocyanide on tinned sheet iron parts of gas meters, has come to the conclusion that this salt has little corrosive effect

Potassium chlorate and sodium chlorate markedly accelerate the solution of tin and tin alloys when they are subjected to attack by mineral acids Watts and Whipple [48] have shown that their accelerating effect is several hundredfold in normal sulfuric-acid solution Eckelmann [49] employed sodium chlorate in a rapid analytical method for the solution of alloys of tin in concentrated hydrochloric acid with the addition of a small amount of concentrated nitric acid

Halla [50] finds that potassium cyanide hinders the corrosion of tin plate

It might be expected that potassium dichromate or sodium dichromate, being strong oxidizing agents, would greatly accelerate the corrosion of tin in non-oxidizing mineral acids As the result of the formation of an insoluble coating on the metal, the tin is protected from further destruction, and potassium and sodium dichromate are thus found to have passivating action instead of accelerating corrosion

Van Name and Hill [51] found as a result of their study of the solution of tin in potassium ferric sulfate and sulfuric acid that when the acidity of the solution was sufficiently high, diffusion became the most important factor in the velocity of the corrosion

Potassium ferricyanide is generally believed to be without corrosive

[45] *J Soc Chem Ind* 22 132 (1903)
[46] *J New England Water Works Assoc* 24 559 568 (1910)
[4] *Gas World,* 69 230 (1918), *Gas J,* 144 359 (1918)
[48] *Trans Am Electrochem Soc,* 32 257 (1917)
[49] *Chem Analyst,* 25 22 (1918)
[50] *J Gasbel,* 56 907 (1913)
[51] *Am J Sci,* 42 301 (1916)

attack on tin It has been used in the conventional Walker or ferroxyl test [52] for the detection of pinholes in tin coatings, especially tin plate The reagent consists of a mixture of 50 parts of gelatin, 450 parts of water, 1 part of potassium ferricyanide, and 1 part of sulfuric acid When spread over a tin-coated surface and allowed to set, blue spots appear at the pinholes This reagent allows us to detect pinholes so small as to be not readily observable by the naked eye

Burns [53] states that a simple and convenient method for finding pinholes in tin coatings on steel consists in immersing the plated part for about four hours in a dilute salt solution containing a trace of hydrogen peroxide The solution is made by adding 5 8 grams of sodium chloride and 3 cc of 3 6 per cent hydrogen peroxide to a liter of water The pinholes are revealed by the development of spots of red iron rust The larger pinholes appear within thirty minutes, and the smaller ones after one or two hours Thus it is possible to get an idea of the size of the pinholes by observing the rate of appearance of the rust spots

Pitschner [54] states that the American Chain Company at Bridgeport, Conn , has developed a very satisfactory modification of the Walker test which consists in the application of the ferricyanide reagent to paper with the ingredients in different concentrations The paper is wetted and applied to the clean surface, taken off in about 2 minutes, and examined for blue spots which are indicative of the porosity of the coating

Potassium and sodium nitrates, in spite of the fact that they are strong oxidizing agents, do not accelerate the solution of tin in alkalies Potassium nitrate itself exerts only a slow corrosion effect

A number of workers agree that acid solutions of potassium permanganate are reduced by tin and cause solution of the metal with roughening of the tin surface The tin is oxidized and the permanganate reduced In their study of the influence of oxidizing agents on the corrosion of metals, Watts and Whipple [55] show that the presence of a small amount of potassium permanganate in a normal hydrochloric acid solution accelerates the corrosion rate almost forty times, while in normal sodium hydroxide the corrosion is only twenty times greater

Sodium acetate affects tin only at a slow rate

Jermstad and Gaule [56] have reported that a 0 35 per cent solution of sodium acid arsenate affects tin with the production of a non-colloidal solution of the metal The normal sodium arsenate, despite the fact

[52] *J Ind Eng Chem*, 1 295 (1909)
[53] *Trans Am Electrochem Soc*, 52 284 (1927)
[54] *Trans Am Electrochem Soc*, 52 283 (1927)
[55] *Trans Am Electrochem Soc* 32 257 (1917)
[56] *Schweis Apoth Ztg*, 57 89-92, 109 113 (1919)

that it is an oxidizing agent, shows no accelerating effect upon the corrosion of tin in sodium hydroxide, although its own solutions cause appreciable tarnish on tin plate

Whittaker [57] finds that tin is a satisfactory material of construction to resist solutions of sodium hydrosulfite The best materials of construction to insure cleanliness of the product are tin, nickel, and monel metal They not only withstand corrosion by solutions and suspensions of the salt itself, but also the other reagents that are met with in the process of manufacture This does not include the first step of the process,—that is, digestion

The Resistance of Tin to Corrosion by Organic Compounds

The resistance of tin metal to attack by organic compounds is quite varied The effect on the metal of various organic acids has been discussed The reactions of tin with the hydrocarbons, both saturated and unsaturated, have been little studied except in the case of acetylene This gas, when either pure and dry or impure and moist, does not perceptibly attack tin metal Acetylene gas in a pure dry state was passed over tin by Reckleben and Scheiber [58] for twenty minutes without any deleterious effect The recommendation has been made that tin be applied as a protective coating to apparatus or metal surfaces which come in continuous contact with acetylene gas Hodgkinson [59] found that tin was unaffected by acetylene at high temperatures

Schonfeld [60] and Hirt [61] attribute the turbidity resulting in beer which has been in contact with tin to the presence of acids contained in the beer or originally in the wort The turbidity is said to be approximately proportional to the acidity, which may be removed by treatment with neutralizing agents such as limestone or calcium carbonate Neutralized beer is without attack on tin and is immune to tin turbidity

Drugs, such as caffeine even up to 20 per cent solution, or caffeine containing small amounts of sodium salicylate, have no solvent action on tin either at ordinary or at elevated temperatures up to the boiling point

When in contact with tin metal, carbon bisulfide, particularly when impure, readily tarnishes polished tin surfaces Beyond a tarnishing effect, the attack is relatively little

Many of the non-ferrous metals react with chlorinated hydrocarbons

[57] *Trans Am Inst Chem Eng*, June, 1923
[58] *Chem Ztg*, 39 42 (1915)
[59] *J Soc Chem Ind*, 37 86T (1918)
[60] *Chem Ztg*, 34 1144 (1910)
[61] *Wochschr Brau*, 27 633-635 (1910)

Berger [62] describes reactions between tin and carbon tetrachloride, hexachlor-ethane, hexachlor-benzol, chloroform, tetrachlor-ethane, and hexachlor-cyclohexane These, as well as other chlorinated and halogenated hydrocarbons, corrode tin metal In many cases the action is accelerated by free acid they may contain, free chlorine, or decomposition products formed by their exposure to sunlight and heat

Tin is readily dissolved and attacked by alkaline pastes which are employed as cosmetics, but it is corroded hardly at all by those materials, such as shaving creams, which are very slightly acid in reaction due to excess of the fatty acids, such as stearic The use of tin in collapsible tubes for various creams, toothpastes, and shaving soaps is well known The average shaving soap is as nearly neutral as possible, and often is found to be slightly acid, due to fatty acids Lead was found by Beythien [63] to be less susceptible than tin to loss in weight.

Formaldehyde, when in contact with tin metal, causes no noticeable effect, but when it is oxidized to formic acid it corrodes tin It is known that when as little as 1 per cent of formaldehyde is present in solutions of the common mineral acids, their attack on steel is markedly lessened, but the same effect does not hold true in respect to tin metal

Jermstad and Gaule [64] found that tin metal was colloidally dissolved when heated for 10 hours in distilled water or 0 5 per cent phenol when the tubes were in rubbing contact The same concentration of phenol has no effect on tin when pieces of the metal are not in contact They found that the following solutions with or without the addition of phenol had no destructive effect on tin metal 1 per cent morphine hydrochloride, 0 01 per cent atropine sulfate, 0 1 per cent cocaine hydrochloride, 5 per cent sodium cacodyl, 0 1 per cent strychnine nitrate, 25 per cent caffeine with sodium salicylate, digalen, 1 per cent novocaine

The widespread use of tinned apparatus in the production, transportation, and preparation of milk leads one to the belief that the metal has been found by experience to be exceedingly satisfactory for this work Milk has practically no corrosive effect on tin metal, irrespective of the length of time during which it is exposed, or the temperature Sour milk readily corrodes tin in tin plate, due to the lactic acid formed Much of the corrosion found in cream-separator parts which are made of stamped sheet steel coated with tin, has been found to be due to lactic acid formed by the souring of the milk left in the separator as the result of careless or insufficient cleaning

Pyridine and pyridine bases have been stated at various times to be

[62] *Compt rend*, 171 29 32 (1920)
[63] *Z Nahr Genussm*, 43 47 55 (1922)
[64] *Schweiz Apoth Ztg*, 57 89 92 (1919)

partially responsible for the corrosion of tinned parts in gas meters and gas lines, although this statement is disputed by some investigators The same holds true for cyanogen and cyanogen compounds

Sugar solutions, particularly in canned foods, serve to protect tin from corrosion by vegetable acids, according to Lehmann [65] and Carles [66] More recent work by the National Canners' Association does not confirm this in all respects

The action of photographic solutions on tin has been studied by Crabtree, Hartt, and Mathews [67] They find that tin and alloys containing tin tend to produce high initial fog when the metal is used as a container for photographic developers This fog later decreases to a normal value when the solution develops better developing powers There is a definite indication of the possibility of the use of a tin alloy or metallic couple which will gradually discharge tin into the developer and act as a preservative of the solution If the tin be in contact with another metal, the fog it creates in the developed plates is materially increased Tin as a metal is one of the least suitable for use as a material of construction for photographic apparatus such as trays, tanks, clamps, and pipes for conveying photographic developers and fixing solutions Practically all the other non-ferrous metals are more suitable In the case of developer tanks, tinned or tin-lined brass faucets should be carefully avoided Tin, solder, or any alloy containing tin should be eliminated from all developing apparatus

EFFECT OF SULFUR

The affinity of tin for sulfur is not very great, although the two elements unite when heated The reaction is vigorous and usually accompanied by incandescence Schutz [68] lists the affinity for sulfur of seven metals in the following order manganese, copper, nickel, iron, tin, zinc, and lead Hydrogen sulfide even in dilute concentrations tarnishes tin metal The discoloration in tin cans has been shown by Mantell and Lincoln [69] to be due to sulfides of tin When moist, sulfur dioxide is markedly destructive of the surface of tin metal, forming some stannous sulfide but also oxidizing the tin to metastannic acid.

Tin metal is slightly soluble in its fused salts, particularly when these are subjected to electrolysis If the temperature of the melt be allowed to drop rapidly, the fused salt fogs as a result of the metal

[65] *Arch Hyg*, **63** 67-122 (1907)
[66] *Bull Agr Intelligence*, 10 621 (1919)
[67] *Ind Eng Chem* 16 13 (1924)
[68] *Metallurgie* 4 659-667 (1907)
[69] *Canadian Chem Met*, 11, (2) 29-31 (1927)

precipitating out of the solution in the form of minute drops, which give the melt a dark color

Effect of Oxygen

It has now been well established that oxygen accelerates and aids the corrosion of tin Jordis and Rosenhaupt [70] have shown that no oxidation of tin takes place at ordinary temperatures, but that the oxidation does begin at 100° C, taking place only at a slow rate Below 200° C tin is oxidized more slowly in moist than in dry oxygen, as a result of the formation of the partially protective coating

Whitman and Russell [71] have shown that the corrosion of tin by weak non-oxidizing acids is determined primarily by the oxygen which is dissolved in the liquid They show also that the presence of hydrogen exerts a retarding influence The following data are taken from their paper

Metal	Acid	Concentration Per Cent by Weight	Average Penetration Per Year			
			Under O_2		Under H_2	
			Cm	Inches	Cm	Inches
Tin	H_2SO_4	6	2 20	0 865	0 018	0 007
	HCl	6	5 69	2 24	0 030	0 012
	HNO_3	3	0 325	0 128	0 320	0 126
	$HC_2H_3O_2$	6	1 18	0 465	0 008	0 003

These figures show over a hundredfold increase with sulfuric, hydrochloric, and acetic acids in low concentrations when saturated with oxygen In the case of nitric acid, the effect of dissolved oxygen is not important because its oxidizing action is overshadowed by that of the acid itself

A summary of the applications of tin in industry as a material to resist corrosion shows its marked utility in connection with the preparation of distilled water where the metal is the preferred material of construction, in apparatus in which food products are made, stored, or preserved, such as tinned kettles and tin cans, in the collection, transportation, and distribution of milk, and in the manufacture and use particularly of the tin-copper alloys, such as the sea-water bronzes, the gun metals, and phosphor-bronze Phosphor-bronze resists the corrosion of sea water better than copper and mine waters better than iron and steel Many of the so-called hydraulic or high-pressure bronzes are markedly resistant to the corrosion action of steam and condenser water The use of Admiralty metal and condenser tubing of copper-tin alloys to resist severe corrosion is too well known to require much comment

[70] *Z angew Chem*, 21 50 66 (1908), *Chem Ztg*, 32 19 (1908)
[71] *Ind Eng Chem*, 17 348 (1925)

CORROSION RESISTANCE OF BRONZES AND THEIR RESTORATION

Many bronzes have resisted the corrosion of ages, having been recovered from graves, bogs, beds of lakes and rivers, buried cities, and from the earth The corrosion crusts of these are generally termed patina, of which there are several kinds malachite, $CuCO_3 \cdot Cu(OH)_2$, atacamite, $CuCl_2 \cdot 3Cu(OH)_2$, and azurite, $2CuCO_3 \cdot Cu(OH)_2$, admixed with silver, stannic oxide, iron oxide, and cupric and lead chlorides These patina are the result of surface attacks by waters which contain oxygen, carbon dioxide, and a greater or less percentage of salts The soluble salts that are formed are removed by solution, while the bronzes become covered according to circumstances with an insoluble layer of either the carbonate or the oxide whereby the form of the objects is preserved

Fink and Eldridge [72] have devoted considerable study to the restoration of antique bronzes Metal corrosion is very strongly evidenced in the ancient bronzes found in our public or private museums Scientists have constantly endeavored, with questionable success, to restore articles so attacked to their original condition Variation in the composition of bronzes is undoubtedly responsible for the lack of a scientific method for cleaning A method which may be successful in restoring one bronze may have no satisfactory effect on another of like composition

There are two classes of bronze corrosion the green crust which coats bronze and other copper alloys that have lain buried in the ground, and the bronze disease, akin to the familiar tin pest The red, green, or brown layers on ancient bronzes are composed chiefly of copper, lead, and tin minerals in the article which have been attacked by the nitrates and nitrides of the soil in which they have lain, forming a crust of copper oxychlorides and oxycarbonates, and tin oxide A layer of copper oxide lies beneath this crust, often covering a core of metal Sometimes the entire mass of bronze is converted to these compounds, leaving none of the original metal in the specimen Moisture of the ground, whether clear water or water containing dissolved salts, is another important corroding agent There are some evidences that former methods of removing corrosion crusts were drastic Some samples show without doubt that strong chemicals such as mineral acids had been applied Others carry the marks of a chisel, denoting the use of crude mechanical means Fink and Eldridge,[73] in their work along these lines, found that the details of design in the original bronze were

[72] "First Report on the Restoration of Ancient Bronzes and Other Alloys," Metropolitan Museum of Art, New York, 1925
[73] *Loc cit*

exactly reproduced in the layer of copper oxide which lies beneath the outer crust Their fundamental idea was to replace cathodically the metal that had gone into the crust, since corrosion is generally conceded to be an electrolytic reaction Experiments determined that the use of a 2 per cent solution of caustic soda as the electrolyte is the safest for this purpose The corroded object, without any preliminary cleaning, is hung in this bath as cathode, totally immersed If the specimen is particularly soft as a result of attack, it is often necessary to wind it in several coils of fine annealed copper wire, or pack it in white sand Anodes of iron, duriron, or platinum are hung on either side of the article The container is generally a glass jar, although large tanks of heavy sheet iron or stoneware may be used, depending on the size of the bronze Low-current densities are preferred The evolution of hydrogen at the cathode will alter the crust to a powdered or spongy copper When the gas is freely given off, the object is removed from the bath and washed by soaking several times in warm water The film of reduced copper is brushed from the specimen, provided the latter was of hard metal under the corrosion crust, or is taken off by means of an acid dip if no core of metal is present The exposed oxide surface, smooth and metallic, preserves all details of design

Some gun metals have shown remarkable corrosion resistance, as is exemplified by the Swedish guns with the inscriptions 1535 and 1632 which were recently salvaged from the sea The bronze had suffered very little corrosion action, although it had been submerged nearly 300 years

The bronzes are attacked by the free halides Alloys with at least 50 atomic percentage of tin are most resistant to the action of hydrochloric acid mixed with ferric chloride, while the alloys corresponding to 80 per cent atomic weight of copper have the greatest resistance to hydrochloric acid alone Sulfuric acid attacks bronze much less vigorously than either copper or tin Ammonia dissolves copper from bronzes containing 1 to 12 per cent tin, but is almost without action on bronze with 25 per cent tin Nitric acid acts less vigorously on bronze than on copper Certain of the bronzes become passive and resistant to corrosion as the result of the formation of a film of stannic oxide

CHAPTER 15

CORROSION OF TIN PLATE BY FOOD PRODUCTS

The problem of corrosion of tin cans by food products which are packed, stored, or canned in these containers is complicated by the large number of factors entering into the situation Tin cans are made of tin plate It is understood that it is an exceedingly difficult matter to form a perfectly continuous coating of tin over the iron base metal

It is commonly conceded that when tin plate is exposed to atmospheric influence, corrosion takes place most rapidly at those points where iron is exposed Small electrolytic cells are set up, and the corrosion of the iron plate is actually accelerated by the presence of the tin When in contact with an electrolyte, iron and tin will function as a battery, iron being the anode and tin the cathode The tendency will, therefore, be for the iron either to oxidize or to disintegrate and for corrosion to be accelerated Corrosion can proceed so far as to actually cause holes to form in the tin plate at those points at which we have uncovered iron

Corrosion of tin plate containers used for food products produces at least three different types of results—first, that which is known as "discoloration" which results in tarnishing, darkening or blackening the bright metal surface of the inside of the container, second, termed "perforation," which results in the formation of holes in the cans to the detriment and spoilage of the enclosed food products (it will be shown that perforation is the result of electrolytic action), and third, that which we shall term "solution," the result of chemical action of the food-product constituents on the metal of the container The resulting action does not usually produce discoloration but makes itself evident in other ways One of the most usual is termed "etching" which is descriptive of the effect It is not meant by this classification that these factors are entirely separate and do not occur together, but it will be shown that they may occur separately without relation to each other, if conditions are favorable, or that they may supplement each other or occur progressively

DISCOLORATION

Discoloration is largely the result of chemical action of the food-product constituents, or resulting products of these, on the metals of

the container If any electrolytic action does occur, it is of secondary importance

It is well known that many food products such as the legumes (corn, peas, beans, etc) contain sulfoproteins These materials, as a result of the processing of the foods in canning, may break down and produce hydrogen sulfide or related compounds Iron is affected by hydrogen sulfide, with the resultant formation of black iron sulfide Tin is also affected by hydrogen sulfide, with the resulting formation of black or brownish-black stannous sulfide With a small amount of sulfides, the effect of the attack on tin may only be evident as a tarnish whose color may vary from blue to brownish black The iron sulfide would be more readily formed, the iron being attacked more readily than the tin

In the case of food products, it is easy to observe the formation of "can black" on the covers of tin-can containers Where iron has been exposed, the black iron sulfide forms readily The attack on tin is less rapid Chemical analysis confirms the statement that can black is iron sulfide The tarnish on tin where iron has not been exposed is stannous sulfide This has been confirmed both by microscopic examination, duplication of similar tarnishes on pure tin by the action of dilute hydrogen-sulfide solution, and by chemical analysis Duplication was done on both electrolytic tin and commercial tin sheet The samples were matched microscopically There is no doubt that to a large extent discoloration is due to sulfide formation

In some of the large number of cans examined, there was a tarnish which was not stannous sulfide but looked like stannous oxide Other sections of the can showed some iron-sulfide tarnish in an adherent layer, usually along the intercrystalline boundary In this connection, the work of Chapman [1] on the action of organic acids on tin is of interest In the absence of air, tin is not oxidized by such acids as tartaric, but, in the presence of air, oxidation of the metal takes place at the surface of the solution, the oxides of tin and stannous tartrate being formed With a restricted amount of oxygen the corrosion product first formed is stannous oxide The stannous oxide first formed may be gradually oxidized further with the production of a brown colloidal material This substance on heating may be converted to the bluish-white hydrated stannic oxide DeFoud [2] reports that dilute oxalic, tartaric, citric, malic, acetic, and lactic acids all attack the tin coatings of cans rapidly in the air, at a slower rate in the presence of restricted

[1] *J   Chem   Soc ,* **103** 775 (1913)
[2] *Pharm   Weekblad,* **55** 498 *et al* (1918)

amounts of air, but scarcely at all in vacuum or in an atmosphere of carbon dioxide All of the acids oxidize more than their equivalent of tin, the main product being stannous oxide or stannous hydroxide It is fairly adherent to the surface of the metal Oxygen has an accelerating action upon the corrosive effect of most reagents on tin

PERFORATION

Sodium chloride by itself does not corrode tin[3] It would not be expected that the saline solutions or strong electrolytes would cause perforation troubles in cans, but that they might have discoloration effects

If a pair of electrodes, one of iron and the other of tin metal, is immersed in the contents of a tin can containing food products preserved in saline solutions, an e m f will be generated The potential is very small and is only indicated on a sensitive millivoltmeter The remarkable happening is that the' voltage will rise to a peak value, fade off, drop to zero, and then build up to a peak value in the reverse direction Mantell and Lincoln[4] observed that the phenomenon of reversal of potential only occurs with those foods preserved in strong electrolytes The term "strong electrolytes" is used from the viewpoint of the theory of electrolytic dissociation The fact that potentials are reversed is indicative that the iron has been passivated, and instead of being as usual, less noble than tin, becomes more noble than tin Instead of functioning in an electrolyte as anode, its position is changed to that of cathode The manner of passivation of the iron is relatively unimportant, it might be caused by a gaseous film, or a thin oxide layer, formed as a result of electrolytic action, or even as a result of chemical action Examples of foods which show the phenomenon of reversed potentials are corn, peas, and beans These do not have perforation effects but all cause discoloration when canned

In contradistinction to those food products which are put up in strong electrolytes, most fruits, berries, etc, are put in sugar solutions These weak electrolytes are of low conductivity and high resistance, while the saline solutions are of high conductivity and low resistance There is no reversal as shown on a millivoltmeter with iron and tin electrodes As a general rule, those foods which do not show a reversal of potential do not give discoloration troubles, but do give perforation difficulties If there is no reversal of potential, the iron has not been passivated, and at exposed spots the iron will be the anode, tin the

[3] Hale and Foster, *J Soc Chem Ind*, 34 464, etc (1915)
[4] *Can Chem Met*, 11 30 (1927)

cathode, and both will be in contact with the electrolyte Galvanic action will be set up, the anodic iron will disintegrate, and, if carried far enough, will cause perforation of the can

Kohman and Sanborn [5] conducted experiments to determine the mechanism of the corrosion of tin and iron, both when in contact and when not in contact, in fruits, and the relation of the results to the electrochemical theory of corrosion They found that in a number of fruits tin is anodic to iron Although not all fruits were studied, the data indicate that this is a rather general condition in canned fruits Many of the facts which did not conform to the older idea that tin is cathodic to iron are readily explained in accordance with these new findings They likewise made electrical measurements which bear out the results of the corrosion tests that tin is anodic to iron The nature of corrosion in fruits is distinctly different from that in solutions of the fruit acids The results are in harmony with commercial experience

For the sake of clarity at this point it is assumed that none of the constituents of the food products in the can can chemically dissolve tin This condition may not exist as such in any actual specific food product In order to avoid electrolytic action and resultant perforation, it would be necessary to have only one metal exposed to the action of the contents of the can If there are two dissimilar metals there will be electrolytic corrosion In the case of tin cans, the only manner by which we can obtain the condition that only one metal is exposed to the action of the electrolyte, is to have the steel surface of the base metal completely covered by tin metal

The work of Kohman in his studies on perforation in the case of Bing cherries, strawberries, and loganberries, shows that oxygen accelerates corrosion, but with the removal of the oxygen, perforation is not prevented Excessive extension of the exhaust with resultant air removal does not prevent perforation Even from Kohman's work the basic explanation for perforation can be seen to be electrolytic Kohman offers the explanation for the lack of hydrogen production in cans of those fruits which develop holes, as being due to depolarizers or oxidizing agents which convert the hydrogen to water

SOLUTION

It is not the usual condition that there is no chemical action on the tin of the tin plate by the contents of the can It is quite usual to have chemical action on the tin by organic acids along with or preceding electrolytic action The corrosion of tin by organic acids has been ex-

[5] *Ind Eng Chem ,* 20 76-79 (1928)

tensively studied by workers who were experimenting without reference to the canning industry Citric, a common fruit acid, definitely etches tin, the attack being most pronounced along the intercrystalline boundaries Malic acid, occurring in apples, readily attacks tin in the presence of air With lessened amounts of air the attack will not proceed as rapidly Acetic acid attacks tin and its alloys While particularly evident in sour milk, lactic acid is also found in other foods

With the exception of canned clams, all canned foods show pH values lower than 7, that is, they are acid in reaction While the effects of the different foods show slight variations, the general results are the same The etching due to peaches is somewhat small, but the detinning action of spinach is quite severe The chemical attack of the acids in spinach on the tin of tin cans has been reported a number of times in the German and American literature The action of pumpkin and squash is quite the same as that of spinach The constituents of rhubarb, grapefruit, and apples markedly attack tin plate It would be expected from what is known of the effects of vegetable acids that the detinning action of cider and berries would be severe in a relative sense This is found to be the case

Perforation troubles are usually associated with those food products containing constituents which chemically attack tin If we were to have a completely tinned sheet free from pinholes and exposed iron, in contact with those foods, we would not expect electrolytic action at first but we would expect chemical attack If the chemical action is continued long enough, enough tin will eventually dissolve to expose the iron of the base metal When this happens, we shall again have two metals in contact with the electrolyte, with the iron as anode and the tin as cathode If there are no neutralizing factors (that is, if the attacking constituent is neither consumed nor brought to equilibrium), no matter how heavy a coating of tin is put on tin cans, perforation will eventually occur

To return to the subject of discoloration This has been shown to be largely due to the action of sulfides and sulfo-compounds Iron and tin sulfides are both black—this is an objectionable color in food products Many metals form white sulfides, an example of which is zinc It is understood that before the advent of the so-called "sanitary" can, the use of zinc chloride flux for soldering the cans effectively prevented discoloration Paper liners in the cans of food products which discolor badly have been effectively used, the paper containing zinc salts

Enameled or lacquered cans have been used, the additional coating

being made on tin plate It is no less difficult to make a perfectly continuous coating of enamel or lacquer on a commercial scale on tin plate than it is to make a perfectly continuous coating of tin on the base steel plate Chemical attack on the tin is usual in the case of those foods which perforate If the enameled or lacquered coating on the tin plate is not perfectly continuous, chemical action of the constituents of the food product, instead of being spread over the whole area of the can, will be localized at those points where the coating is not continuous and the tin plate is exposed With localized action, corrosion will be accelerated and perforation will result more rapidly than in an unenameled can Commercial experience has shown that enameled cans perforate more readily than those which are not enameled

There seems to be a definite field for containers in which tin is absent, that is, a container made of sheet iron with an enameled surface If the enameled coating on the steel plate were not continuous, the exposed iron would be chemically attacked and rusted The commercial feasibility of making such a container with a minimum of uncovered iron spots is an open question How much rusting would occur in cans made of enameled sheet steel or how objectionable this rusting would be is not known A large number of tinless cans have been used for fish products The cans stood up very well The food products were preserved in better condition than in ordinary cans

C-Enamel Lined Cans

There has been one major improvement in containers, namely, the development of what is known in the industry as the "C-Enamel Lined Can " This C-Enamel was developed primarily to prevent iron-sulfide discoloration in canned corn, and for this purpose it has been eminently successful It has also been found that C-Enamel will prevent iron-sulfide discoloration with clams, lobster, shrimp, and crabmeat

C-Enamel is made by specially baking plate, under very accurate heat control, that has been coated with a lacquer composed of oil and gums that have been specially treated and mixed with an exceedingly small amount of zinc oxide The small amount of zinc oxide present is completely imbedded and protected in the enamel, so that practically none of it comes out into the canned food The total amount in the enamel is so small that even if it all came out in the food, the Bureau of Chemistry's tolerance for zinc in foods would never be reached This C-Enamel is designated only for non-acid foods and cannot be used with acid foods, as acid will disintegrate the enamel The regular enamel used with acid foods is of entirely different character

Dr G S Bohart, a chemist with the National Canners Association, Washington, D C, discovered and proved the efficacy of a minute amount of zinc oxide in a coating medium A patent was taken out in his name and made available to the industry Commercial can-makers have developed C-Enamel on the basis of his discovery

VALUE OF TIN AS FOOD CONTAINER

Although much of the foregoing would seem to justify the conclusion that the tin can leaves much to be desired as a perfect container for preserving foods, it is well to remember that there is not available at the present time as good a substitute which has all the commercial features of the tin can Glass containers would eliminate corrosion, but they are not suitable or adaptable for cheap shipping and transportation Paper containers will not oidinarily stand processing of foods Metal containers other than those made of tin plate bring along their own corrosion problems They are also more costly Tin cans are relatively cheap because of the quantities in which they aie made and consumed

Commercially, it is to be observed that even with its defects the tin can is adapted to a great many different food products Food product losses due to can failures bulk very large in actual money, although the percentage of cans failing is low. An estimate of the size of the industry can be gained from the fact that approximately 8,000,000,000 cans per year are used in the United States

A factor to be considered in tin cans and their use is the thought that in many cases the use of tin in cans is decorative At other times it is, or should be, protective

Baker [6] summarizes the situation with respect to the use of tin cans in the canning industry in Table 18

TABLE 18
RELATIVE VALUE OF TIN CANS IN THE CANNING INDUSTRY *

Product	Relative Value of the Tin Can as a Container
Vegetables	
Peas	Practically a perfect container
Tomatoes	No trouble when the article is properly prepared, closed, and cooked
Tomato pulp and paste	Tin cans are very satisfactory as containers
Corn	Very considerable difficulty was formerly experienced from discoloration by the formation of iron sulfide by the action of sulfur from the corn on the iron of the steel base There is no longer any necessity for the iron sulfide discoloration in canned corn, as

* This table has been amended by private communication from H A Baker

[6] "Status of the Tin Can in the Canned Food Industry," New York, American Can Company, 1923

TABLE 18—*Continued*

Product	Relative Value of the Tin Can as a Container
	it has been found during a period of years that it can be completely prevented by the use of C-Enamel cans Practically all of the higher grades of corn today are packed in C-Enamel cans, and a very large proportion of the standard corn is also packed in the C-Enamel can Apparently it is only a question of time when no corn will be packed in any other kind of container
Baked beans and red beans	Ideal
Asparagus	Very satisfactory
String beans	Eminently satisfactory
Hominy	Trouble from discoloration, not a defect inherent in the tin
Sauerkraut	Ideal
Tomato and other soups	No ground for complaint on any score
Sweet potatoes	Discoloration, resulting from improper preparation, not attributable to the tin container
Spinach	Hard product to hold in a tin can, special preparation of the product is necessary, detinning action is rather severe
Lima beans	Very suitable
Succotash	Very little trouble experienced
Okra	A great deal of trouble with discoloration unless special methods are used
Spaghetti	Eminently satisfactory
Pumpkin and squash	Severe dissolving action on the tin coating and the contents of the can are affected An enameled can is highly satisfactory
Beets	Difficulty in preserving the color, an enameled can must be used
Fruits	
Pears, peaches and apricots	Almost ideal
Pineapple	Eminently satisfactory
Prunes, grapes, raisins, figs	Eminently satisfactory
Ripe olives	No difficulties experienced
Rhubarb	Unsatisfactory except for a short period of time
Grape fruit	Special precautions in preparation are necessary, not satisfactory for long periods
Apples	Trouble was formerly experienced in perforations of the can Some of this trouble is attributable to method of preparation of the product Soaking and steaming methods have been developed to the point where perforations no longer seem to be commercially significant
Cherries	
White	Very little trouble experienced
Black	"Probably the most severely perforating article ever packed in a tin can"
Red, sour	Much trouble from perforations, some of which is attributable to improper preparation Charcoal tin plate should be used, an enamel coating is necessary to preserve the color
Apple butter	At the best, only a temporary container Heavy tin coatings should be used
Jams and preserves	Very little difficulty experienced
Plums	Same as red cherries.

TABLE 18—*Continued*

Product	Relative Value of the Tin Can as a Container
Berries	
Strawberries	Not a satisfactory container The chance of perforation is very high Enameled cans of charcoal tin plate should be used
Blueberries	Much the same as strawberries Enameled cans are not necessary to preserve the color
Huckleberries	An enameled can must be used to preserve the color, but the chance of perforation is very great
Cranberries	Should be regarded at best as a semi-perishable article
Black raspberries	Fairly good results, if not kept too long
Red raspberries, logan-berries	Reasonably safe to can Enameled cans must be used to preserve the color and charcoal plate will give assurance of added safety
Canned sirup	Considerable trouble experienced, but on account of improper preparation, the tin plate itself gives no trouble
Cider	The cans are readily perforated Unsatisfactory
Salmon	Excellently adapted for this product At the present time a very large proportion of the pack is sealed in vacuum The preheating by exhaust boxes has been largely discontinued
Oysters	Satisfactory
Clams	Formerly gave trouble on account of discoloration The tin plate and can not at fault The use of C-Enamel cans prevents iron-sulfide discoloration (see corn)
Sardines	No trouble attributable to the use of tin cans At the present time practically all sardine cans are sealed with a lining compounds in the curl of the covers, so that hermetic sealing is possible and seepage of oil is prevented Formerly no sealing medium was used in the curl of sardine can covers
Tuna fish	Satisfactory, with improved canning methods now in use
Lobster	Some trouble from discoloration caused by iron sulfide The C-Enamel can will practically prevent the trouble, although in this case with the dry product the results cannot be described as absolutely perfect
Shrimp	Satisfactory for the "wet pack" The C-Enamel can prevents all formation of iron sulfide in wet pack, and in the "dry pack" iron-sulfide formation is also practically controlled, although with this dry product there may be at times slight signs of iron-sulfide formation, as the enamel is not so efficient when liquid is not present The C-Enamel can will not prevent the formation of a certain amount of rust with dry pack shrimp, but this can be prevented by sealing the can in vacuum
Canned meat	Much of the trouble which has been experienced can not be attributed to the tin plate Heavy grades of tin coating should be used
Canned milk	Such trouble as has been experienced is not attributable to the tin plate

CHAPTER 16

SECONDARY TIN

Tin drosses, ashes, and at times slags result from many commercial operations such as wire coating, tin-plate manufacture, hot-tin dipping, copper-sheet coating as examples The discussion of the metallurgical treatment of the drosses can not be limited to tin alone, since residues of this sort are ordinarily not available in sufficiently large quantities to permit continued and efficient tin production from them as a raw material Tin ashes are quite generally treated with solder drosses and other lead residues containing considerable amounts of tin In the majority of smelters, the final products of smelting are lead-tin alloys of widely varying proportions These are worked up into alloys of commercial application

The residues are smelted in either blast or reverberatory furnaces, in a manner analogous to the methods employed for tin ores The reverberatory has generally proved to be the more advantageous type, although the blast furnace is very definitely applicable to handling lead-tin alloys containing 40 to 50 per cent tin Small-grained powdered materials, such as most drosses are, must be either briquetted, slagged, or sintered before being charged into a blast furnace, otherwise the dust losses will be very high The volatilization and mechanical losses are high in blast furnaces Blast furnaces are often preferred for treating reverberatory residues rich in tin and tin alloys by alloying through the use of iron or lead

Blast-furnace Smelting

The structures employed for tin-residue smelting are much lighter than the blast furnaces used for ore smelting Figure 90 shows a commercial type, with the small forehearth to receive the product of the furnace Usually the structure is only a fireclay-lined steel shell The forehearth usually is divided into two sections by a partition, with a slot near the bottom connecting the two sections The bottom slot is kept covered with metal to prevent slag from closing it The forehearth serves as a settling device when slag and molten metal are discharged from the furnace The slag remains in the forehearth, the metal rises

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Reverberatory-furnace Smelting

When tin ashes and residues are smelted in reverberatory furnaces, many of the disadvantages of the blast furnace are eliminated The usual furnaces are small, having hearths 7 to 10 feet long and 5 to 6 feet wide, with a hearth slope about ½ inch per foot The concavity of the hearth is about 5 to 7 inches total

Tin has a much stronger penetrative action on the brickwork of the furnaces than lead The hearth is usually composed of four layers of bricks, the top layer of which is made up of high-quality fireclay bricks standing on end The second layer of bricks, laid sideways, are also of high-grade material, while the two lower layers are of ordinary fireclay bricks laid flat

The hearth is laid upon heavy cast-iron plates extending about 2 inches beyond the brickwork of the furnace on three sides

The bottom plate rests upon heavy girders stretched across a cellar or vault cooled by outside air Cooling of the bottom plate will prevent too copious a flow of tin through the hearth, or even freeze up the tin penetrated to the bottom plate

In treating tin ashes and residues containing metallic oxides almost exclusively, reverberatory practice does not necessitate slag forming materials Metallic iron is usually removed in advance by magnetic separation Residues containing considerable percentages of metal, such as skimmings, sweepings, and dross, should first be treated in melting pots or liquating furnaces to remove as much metal as possible

If the residues for treatment contain considerable quantities of sulfur, arsenic, iron, copper, or antimony, they are given a combined roasting and liquation treatment in a reverberatory furnace They are changed into a hard, powdery material, which is added to tin ores or other tin materials smelted in blast furnaces

The liquating treatment has been replaced by a segregation process Charges of 4 or 5 tons are treated in a reverberatory furnace in small lots of about 500 pounds each until the furnace is half filled with metal The ashes collected on top of the metallic bath are then drawn off Fresh drosses are charged until the furnace is almost filled with metal After removing all of the ashes, the metal is heated to a temperature of about 1450° F Arsenic is removed by washing the metal with thin iron scrap The temperature is gradually raised to 1550° to 1600° F The metal is puddled for about ten minutes in order to remove any zinc and sulfur present

The metallic bath is now cooled down as rapidly as possible, firing
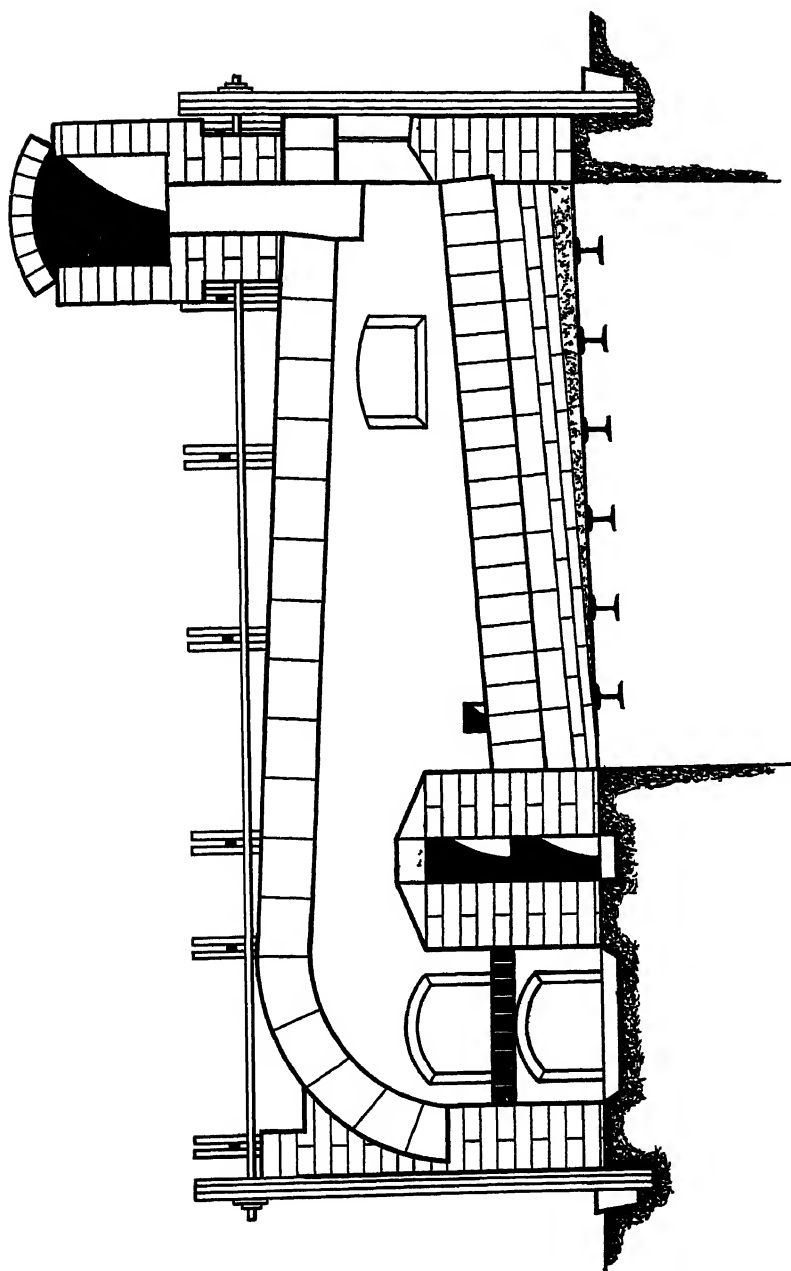
Fig 91 —Tin smelting reverberatory furnace

being stopped All working doors are opened When a hard crust about 1 inch thick has been formed, the white metal below is tapped and cast into molds

The process is concluded by again heating up the furnace until all of the white metal adhering to the dark crust has been liquated The residues are removed and treated in blast furnaces

Tin and tin-alloy ashes, immediately previous to charging, are mixed with about 12 to 15 per cent of powdered magnesite and moistened in order to prevent excessive dusting After charging, the furnace is closed and luted tightly and the temperature slowly raised to 1850° F About 1 hour after reaching this temperature, the material is rabbled thoroughly, 2 or 3 shovelfuls of ground anthracite added, the charge again spread out, and heated for another half hour Treatment is continued until the hearth has filled with a bath of metal In rabbling, care must be taken not to stir up the molten tin more than absolutely necessary A reducing atmosphere must be maintained in the furnace The metal should be tapped at the end of the treatment of each charge

In contrast to the smelting of tin ore, the reverberatory furnace method of smelting tin residues is comparatively simple if the high temperatures necessary are maintained If the slag produced be too viscous for satisfactory treatment, a little fluorspar may be added

The semi-melted residue remaining on top of the metal at the end of the process is mixed with a small amount of lime, the mixture rabbled for a few minutes and exposed to the full heat of the furnace about 30 minutes The greater part of the mechanically suspended metal in the residues in form of prills is liberated Too large an amount of lime will destroy the slaggy nature of the residues They then become dry, powdery, and unsuitable for blast-furnace treatment

"Tin ashes" produced in the Harriss lead-refining process contain about 5 to 15 per cent of tin, the exact amounts of tin depending upon the percentages of tin contained in the lead and upon the speed of oxidation If this material is treated with the object of extracting both tin and lead, comparatively high temperatures and strongly reducing conditions must be maintained However, if the smelting is carried out below 1500° F and in a neutral or even slightly oxidizing furnace atmosphere, 5 per cent of ground anthracite is the only reducing agent needed for satisfactory results

In dip-tinning plants, excess tin on the tinned objects is whirled off mechanically or shaken off on the floor immediately after the object comes out of the tinning pot These are swept up and treated, with the drosses and skimmings from the pots, in cast-iron melting pots

Considerable flux (zinc chloride) is contained in the skimmings and sweepings The pot is of two sections, divided by a partition with a slot connecting the two sections On the higher side, the skimmings and sweepings are chaiged, the metal melted from them, and ladled out on the lower side The residues remaining are leached with water to recover the flux, centrifuged to clarify the flux solution, and the separated slimes smelted for tin-metal recovery

CHARACTERISTICS AND USES OF SECONDARY TIN

The tin alloys produced in the reverberatory- and blast-furnace processes are chiefly lead-tin alloys containing 20 to 75 per cent tin Those containing up to about 35 per cent tin are used for the manufacture of ordinary lead-tin or lead-tin-antimony alloys Products with more than 35 per cent tin are employed for the production of "tin alloy" and alloys rich in tin used as base alloys for the manufacture of tin solders and high-grade bearing metals

The liquation process may be used in concentrating the tin contents of alloys containing more than 60 per cent of tin The melting point of the tin-lead eutectic containing from 55 to 62 per cent of tin (depending upon the amount of antimony and other impurities present) is 360° to 365° F If, therefore, a material containing, say, 70 per cent of tin is deposited on the inclined hearth of a reverberatory furnace and carefully heated to a temperature of about 370° F , the eutectic alloy will be "sweated out "

CHAPTER 17

DETINNING OF TIN PLATE SCRAP

EARLY DETINNING PROCESSES

As the tin plate industry grew to large proportions, the problem arose as to the disposal of clippings and other scrap which accumulate in large quantities Tin plate scrap, made as a result of working up of tin plate into cans, boxes, containers, etc , has been the subject of much study In its plated state the scrap cannot be puddled or charged into the open hearth furnace The tin coating prevents a satisfactory iron or steel product being made Hundreds of patents in all the different industrial countries have been granted for the removal of this coating The tin coating has a considerable value, either as metallic tin, or as tin salts, used in various industries

The problem at first did not appear to be very difficult The can factories were glad to give their scrap tin plate away simply to get rid of it Decades of study and experimentation were required before a feasible method was developed, which yielded sufficiently valuable commercial results

Many of the chemical and electrochemical processes were failures, as were most of the mechanical processes, either because the acids used attacked the iron as well as the tin, or because they would not dissolve the tin sufficiently and left a considerable part adhering to the iron It was found in many cases that the chemicals used were too expensive to make the process an economical one Three processes, however, have operated successfully and have been more or less in competition with one another for the last forty years, during which time one or another has alternately gained preponderance, due to refinements in that process over the others These three processes are the electrolytic alkali process, the alkali chemical process and the chlorine process For its historical value the acid electrolytic process will be included

As far back as 1876, Keith[1] recommended the electrolysis of tin scrap in an alkali solution, while in 1882 Thomas Goldschmidt, in Germany, conducted experiments with a warm solution of caustic soda, using the tin plate scrap as the anode and an iron plate as the cathode

[1] U S Pat. 176,658

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This simple idea has been the basis for the further development of the industry The operation on a plant scale offers difficulties, both electrochemical and mechanical, which have been solved in commercial operation

The tin is recovered at the cathode in the form of a spongy or finely granulated precipitate, which can be removed and melted The process yields a serviceable iron in a single operation, which may be compressed into solid billets, and for which a market can be readily found The apparent simplicity of the method caused it to come into quite general use in a comparatively short time, so that up to about 1907 it dominated the entire field

ALKALINE ELECTROLYTIC DETINNING

Some of the most successful detinning plants in operation use the alkaline-electrolyte process This method consists essentially of electrolyzing the tin plate scrap at the anode in a bath of caustic soda and depositing spongy metallic tin at the cathode

Even before the first proposals found their way into the patent literature, alkaline electrolytes were employed in the Goldschmidt chemical works at Essen on the Ruhr, Germany, and were later introduced into the plants of the Electrochemische Fabrik Kempen on the Rhine and of H W Von der Linde at Crefeld and into other smaller works in Germany, Holland, and England

The tin plate scrap serves as the anode in the cell, the cathodes are either steel plates or the sides of the steel tanks Iron is the cheapest and the most generally used electrode material The tanks are connected up to the negative conductor, while the positive part of the cell is connected to copper bars or tubes which are placed on insulated supports lying along the edges of the tanks The baskets are charged with tin plate scrap and are of suitable size and dimensions so that they may be handled with ease The baskets are made of heavy iron wire gauze of wide mesh, bound with strong heavy angle-iron bands The bands extend up from the basket and are bent into hooks above, which rest on and make contact with the positive bus bars The basket design is usually on the basis of about 3 to 3½ pounds of scrap per cubic foot of basket volume Baskets fit the tanks rather closely, with enough clearance between the sides of the baskets and the inner walls of the tanks or the cathodes to prevent electrical short circuits The capacity of baskets bear about a 3 5 relation to the volume of the bath The electrical resistance of the electrolyte is thus kept as low as possible The baskets are suspended side by side If an increased cathode

area is needed, iron plates are hung between each pair of baskets This is considered better practice More careful control of the bath is then required The nature of the tin plate scrap and the impossibility of charging the anode baskets uniformly on a large scale, although equal weights may be electrolyzed, make it impossible to provide a constant anode area per bath The current conditions are constantly changing Control, at best, is always difficult

The pipes carrying the electrolyte from and to the tanks are insulated, and connected with the main conductors Circulation of the electrolyte is essential The discharge pipe is provided with a screening arrangement and an overflow for the purpose of holding back suspended particles of spongy tin Diaphragms are not used in commercial practice

The scrap is constantly moved and loosened by iron forks during electrolysis Thus the electrical contacts are well made and no permanent resistance is offered to the current It is most important that the tin plate scrap be thoroughly loosened, so that the electrolyte may reach the middle of the basket readily The scrap must be as far as possible immersed in the solution

Better results and speedier stripping are obtained with baths at 60° to 70° C At this temperature there is about 5 per cent evaporation of liquid per 24 hours The water lost by evaporation is replaced by the addition of hot water to the electrolyte

With the solutions as hot as possible, they should be as high in free soda and as low in stannates and carbonates as operation will allow Periodic regeneration of the electrolytes is necessary, as the stannate and carbonate content builds up, also to reduce the iron and lead compounds as well as soaps formed from the resins, lacquer, and fatty materials introduced with the scrap The electrolytes take up but little iron and lead unless they contain chlorides

The whole of the caustic does not remain in the free condition during electrolysis Even without the aid of the current, especially in the presence of atmospheric oxygen, it would dissolve the tin with formation of stannites and stannates As open tanks are used, carbon dioxide will be adsorbed The higher the free caustic concentration in the solution, the more rapid will be the absorption of the gas, with resulting formation of carbonates

Work is begun with a solution containing at most 9 per cent sodium hydroxide (7% sodium oxide) This quantity is maintained throughout the process The caustic is on the average distributed as follows among the compounds formed during electrolysis

3-3 5 per cent sodium oxide, free as hydroxide

1-1 5 per cent sodium oxide, combined with 3 per cent stannous oxide (2 34% stannate) as stannate

1 7-2 8 pei cent sodium oxide combined with carbon dioxide as carbonate

When a larger proportion of carbon dioxide than the above is taken up, stannic acid is precipitated in the baths, so that regeneration of the solution becomes necessary

The time necessaiy for the complete detinning of the scrap is dependent not only the current employed but also on the tin content of the scrap, the temperature of the electrolyte, the strength of the electrolyte, the number of baskets per cell, and the quantity of scrap per basket These factois differ so much in different works that it is usually stated that the detinning takes anywhere from 2 to 7 hours for completion Under normal conditions in one plant handling scrap of 1 7 to 2 0 per cent tin content, with six baskets to the tank, each basket filled with about 75 pounds of scrap, at a current density of about 10 amperes per square foot, detinning was completed in 3 hours when electrical contacts were good With higher current densities the scrap baskets must be changed more often, but on the other hand, the effectiveness of the bath is utilized to a greater extent

With any chosen density, knowing the weight of scrap in the bath and its tin content, the time of detinning can be calculated, as one ampere hour dissolves about 1 1 grams of tin More tin is dissolved off the anode than is deposited on the cathode, so that the concentration of stannite and stannate in the solution increases during its use

The dissolved tin is precipitated as oxide by bubbling carbon dioxide through it (carbon dioxide from waste furnace gases, motor exhausts, etc) and the stannic oxide is recovered by filtration, washed, and dried either to be sold as such for use in ceramic work or smelted to metallic tin The electrolyte, now free from tin and saturated with carbonate, is causticized by the use of lime Iron in the electrolyte is precipitated along with the calcium carbonate formed The regenerated solution, after being restored to the proper concentration, is returned to the system for reuse The following operating conditions hold good in one modern plant

Current—1,500 amperes
Cells—6 baskets per cell, 70-75 pounds of scrap per basket
Electrical connection—6 cells in series, 9-12 volts across the system or about 1 5 volts per cell
Scrap—2 per cent tin approximately
Operating time—22 hours per day, 350 days per year

Detinning time—3 hours, entire set of baskets per cell changed
Detinned scrap—0 1 per cent tin
Output—3,000 tons detinned per year, 47 5 tons tin produced per year

Of the 1,500 amperes in the system, about 80 per cent of the current was useful in detinning, the rest being consumed in side reactions and polarization counter effects

The insertion and removal of the scrap baskets in the electrolyte take place in a regular and systematic manner The completion of the detinning can be checked by the change in color of the scrap from its original appearance to colors varying from blue black to red brown

The detinned scrap is allowed to drain from the electrolyte and is washed with water The material is then dumped out of the baskets, dried, either compressed or baled for shipment, or sold as it is

At intervals the tin sponge is removed from the cathode plates by iron scrapers, the cathodes being lifted out of the cells at the time The sponge tin is washed free from alkali by more or less violent agitation with water It is then a granular material It is dried by centrifuging and melted to massive tin In some works the washed and dried tin is compressed before melting

Tin-bearing slimes at the bottom of the electrolytic baths, resulting from particles falling off the cathode or anode, and material dropping into the bath when the cathodes are scraped, are produced This material contains tin, sand, iron, and alkali and various organic substances introduced into the bath through dirt on the scrap The slimes are recovered by draining them off at intervals, adding them to slimes resulting from the detinned scrap washing tanks and the tin oxide produced by regenerating the electrolyte The whole mass is smelted for tin

Often in handling dirty scrap the bath will become contaminated through lacquer, grease, oils, and soaps formed as a result of the action of the caustic on organic matters At the time of regeneration of the electrolyte it is usual to remove these materials by cooling the electrolyte down to a low enough temperature so that they separate out

The detinned scrap, containing, under good operation, less than 0 1 per cent tin, is quite suitable for the manufacture of open-hearth steel

Many methods have been suggested for the recovery of tin from tin-plate scrap in alkaline baths with the aid of the electric current Many of them have had only small development and quite a number after being in operation for some time have been abandoned in favor of the straight caustic bath

Borchers proposed to use a 12 to 15 per cent solution of common

salt, containing 3 to 5 per cent sodium stannate as an electrolyte In consequence of the high conducting power of the solution, this electrolyte serves much better than sodium stannate With 5 to 15 amperes per square foot and a potential of 2 to 3 volts, he obtained a spongy metallic tin cathode deposit with a bath temperature of 40° to 50° C (104° to 122° F) The deposited material was washed, dried, melted, and cast The bath had to be kept distinctly alkaline, as the quantity of tin oxide in the bath increased, more alkali had to be added Toward the end of the process the solution became so concentrated that it was more profitable to work it up for preparing salt, by evaporating to dryness, than to continue to electrolysis The advantages claimed by Borchers were practically complete removal of the tin from the clippings, the production of a residue of clean sheet iron, the possibility of producing an iron-free tin, the practicability of using the iron vessel as the cathode, and the use of an iron basket as the anode The commercial development of this process has been very small

In Keith's process a solution of sea salt and caustic soda is used as the electrolyte Iron tanks are used, the walls of the tanks acting as cathodes, with the scrap in baskets as the anode

Beatson's process used a hot solution of soda with potassium cyanide added Iron plates or the walls of the iron-tank containers were used as cathodes Alkaline solutions of cyanides decompose readily when heated to the boiling point and kept there The process has little to recommend it

Price and others used solutions of caustic soda as the electrolyte

Walbridge's process used a solution of caustic soda with an oxidizing agent, as sodium nitrate Weber's process [2] is quite similar

H Goldschmidt [3] provides for detinning by the use of sodium hydroxide or sodium-stannate electrolyte and passes high amperage currents in parallel through several batches of scrap at the same time

Electrolytic detinning has not progressed in recent years because of the rapid advances of the chlorine-detinning method The chlorine method is now of greater importance It is much easier to operate, much cleaner, more efficient, and produces more valuable materials finding a very ready market Sodium stannate, a by-product of electrolytic detinning, finds employment in tin-plating baths, but the total tonnage consumed is very small in an oversupplied market

A process of considerable commercial importance is that of detinning with alkalies, with or without the aid of oxidizers This method

- U S Pat 1,018,734
³ U S Pats 1,160,400 1

was practised at an early stage of the industry, but did not always remove a sufficient amount of tin, with the result that a considerable part was left on the iron It is only within recent years that this process, using alkali and saltpeter, has been developed to a point where the results compare with the product of the chlorine process

In this process the scrap is cleaned very carefully and is then placed in a well-heated solution containing a considerable excess of free alkali and saltpeter or other oxidizer The mass is then kept at a boiling temperature for several hours, during which the tin reacts to form sodium stannate which accumulates as crystals These crystals are drawn off and subjected to centrifugal action while the remaining mother liquor is diluted with the necessary caustic and saltpeter to enable it to be used again in the same way as the original solution

The stannate is subjected to further treatment by dissolving in water and precipitating tin oxide by means of sodium bicarbonate It should be borne in mind that the alkali used in this process is always recovered and used over and over, so that only a small loss results The saltpeter is also recovered at the end of the operation, with the exception of the amount required for the oxidation of the tin

The tin oxide obtained in this process is used extensively as a coloring matter in the enamel industry or is smelted in reverberatory furnaces to form pig tin The Goldschmidt Detinning Company uses this process in addition to the chlorine process in its various plants

ACID ELECTROLYSIS

Among the acid electrolytes for detinning, use has been made of sulfuric acid, hydrochloric acid, acid sulfates, and chlorides Gutensohn patented the use of sulfuric acid Most of the acid electrolytes are only of historical interest now

The old Siemens and Halske process, using a sulfuric-acid solvent for the detinning of scrap by electrolysis, is no longer in operation This was practically the only one ever used commercially By the treatment of 6 tons of scrap per week, there would be obtained about 28 tons of crystallized ferrous sulfate in addition to the metallic tin recovered. It is doubtful whether the ferrous sulfate obtained would even repay the outlay on the sulfuric acid used, as green vitriol is produced as a by-product in many other metallurgical industries and is thrown on the market in large quantities at a very cheap rate It is evident that if it were intended to strip the tin completely from the scrap by

⁴ German Pat 12,883

electrolytic means in a sulfuric acid bath, an enormous quantity of iron would be dissolved and pass into the solution

Other than the old Siemens and Halske process, there has been little commercial use made of acid electrolytes, largely because of the quantity of iron of the scrap that is unavoidably dissolved in the electrolyte After some time the electrolyte becomes unfit for use and must be renewed, with or without recovery of the iron compounds it contains, the compounds being recovered as commercial iron salts In this process the tin is deposited as a sponge on the cathode as long as the solution is acid, but as the bath becomes more and more neutral the deposit becomes pulverulent and in some cases crystalline

Chlorine Process

The chlorine process was first taken up by Higgins in 1854, in England,[5] and later by Parmalee,[6] Seeley,[7] and Panton[8] in the United States

In 1883 there was a plant operating successfully, using the chlorine process, at Metikon, on Lake Zurich, Switzerland A fixed iron cylinder, 13 feet (3 96 m) high, of 39 inches (99 cm) diameter, was used The cylinder had a perforated false bottom on which the cuttings were placed, and through the openings of which the chlorine gas passed and came in contact with the clippings The stannic chloride which was formed collected as a refining liquid in a receiver under the cylinder

Further progress was made in chlorine detinning in 1885, when Lambotte, in Brussels, started to operate on a large scale with a shaft furnace filled with tin scrap from the top, while chlorine gas, strongly diluted with air, was introduced at the bottom The air carried away the stannic chloride to the condensers, where it was condensed as a watery solution of the stannic chloride The detinned clippings were then removed from the bottom of the furnace and compressed into billets

A chlorine detinning plant was established in New York in 1873, operating according to the Seeley patent, but the concern failed when the financial panic of that year brought ruin to many concerns

It was not until 1907 that the chlorine detinning process gained real importance In that year Thomas Goldschmidt, one of the pioneers in the detinning industry, abandoned the electrolytic process entirely in favor of the chlorine process which he had developed Since then

[5] English Pat 766 (1854)
[6] U S Pat 102,148
[7] U S Pat 127,375
[8] U S Pat 135,578

the chlorine process has grown rapidly, and today there are immense quantities of tin scrap and old tin cans detinned by this method

Some of the basic conditions of chlorine detinning had been correctly observed by the early experimenters, the most important of which is that all humidity must be excluded in order to avoid any corrosive action of the chlorine on iron It has also been found that the material must be free from all organic substances, such as paper, straw, varnish, etc

Chlorine gas will combine with tin, under the development of considerable heat, to form anhydrous tin tetrachloride This is a heavy liquid which fumes strongly in air It has been known to chemists for about 300 years In fact, as early as 1605 Libavius described this product, and ever since that time it has been known under the name of *liquid fumans Libavii* By cautious addition of water to this fuming liquid, solid stannic-chloride crystals were precipitated and sold in that form to be used in dyeing

The thermal datum of the reaction is

$$Sn + 2Cl_2 = SnCl_4 + 127,250 \text{ cals}$$

The heat of formation of stannic chloride is given by various authorities at from 127,250 calories to 129,600 calories The heat of a solution of stannic chloride is 29,920 calories It has a density of approximately 2 29, a melting point of $-33°$ C, and a boiling point of about $114°$ C It dissolves readily in water, forming a solution from which the hydrated stannic oxide separates on boiling or standing

In the operation of the chlorine-gas process all the following precautions must be observed, and must be strictly adhered to in order that the operation may not be a failure

Perfectly dry chlorine gas or mixtures of chlorine and other gases only can be used Moisture even in small quantities is detrimental to the process Only dry clippings can be detinned The clippings must be clean Chlorine will only slightly detin dirty, greasy, or oily clippings The process cannot be used for unclean tin plate scrap

Provision must be made for keeping the temperature of the reaction chamber below $38°$ C or $100°$ F, otherwise the iron of the chamber or detinning vessel will be affected by the chlorine to form ferric chloride Chlorine also acts on the iron in the presence of water, the ferric chloride formed accelerating the attack of the chlorine on the iron

The chief difficulty of this process was that the iron scrap was exceedingly liable to rust, as was the case with all former processes of detinning with chlorine Even if all moisture were carefully avoided

and the resulting steel-gray iron were stored in a very dry place, it would rust and the resulting corrosion would quickly spread It was found that chlorine is not absolutely without an attack on the iron, but forms a thin invisible film of anhydrous ferric chloride, which will attract water from the air, forming oxychloride, this is again reduced by the iron, forming more rust The corrosion of the iron was prevented by removing the ferric-chloride film by a washing process

The most important modifications of the chlorine process are those of Goldschmidt, Sperry, Acker, and Von Schutz There have been manifold and multitudinous methods and apparatus proposed and used, for practically all of which patents have been granted The same result can be obtained in many different ways

In the Goldschmidt process, chlorine is introduced into the detinning chamber under pressure The dry tin scrap is put into large cylindrical containers, either in more or less loose form or compressed into baskets These containers, after being filled, are closed tightly Dry chlorine is then introduced The heat of reaction of the chlorine on the tin is dissipated by outside cooling of the reaction chamber After detinning has been completed, the remaining gases are drawn off by suction, along with any volatilized stannic chloride, and the detinned bales of scrap washed and dried The detinned scrap is then ready for sale

Pressure is used in the Goldschmidt process to cause the reaction gas to penetrate all parts of the scrap material in the reaction cylinder When the gaseous chlorine forms liquid tin chloride, the pressure is reduced due to the decrease in volume of the gases As long as the pressure continues to drop, detinning is taking place When the pressure remains constant for some time, it is evident that the chlorine does not find any more tin with which to combine This is a sure indication that the detinning is completed

It is stated that the pressures employed in the Goldschmidt process are about 3 7 atmospheres (54 lb per sq in) at 0° C, and 7 6 atmospheres (112 lb per sq in) at 25° C

In the method of Von Schutz a dry mixture of chlorine, diluted with other gases (as dry air), is drawn through the scrap by suction Any inflowing gases which are too cold can be preheated by being passed through pipes around which exit gases of the process are drawn off, these exit gases being heated by the heat of the detinning reaction The vacuum is produced in part by the cooling and contraction in volume of the exit gases Little trouble is experienced with clogging of the pipes, due to the deposit of stannic chloride

The detinned scrap is washed in the same cylinder in which the de-

tinning was done, and drying is done in place, after washing, by blowing hot furnace gases through the tin scrap bales in the detinning chamber The finished material is removed from the chamber and sold

The Von Schutz process has the advantage of having a shorter detinning time, simple apparatus, and little manual handling as the detinning, washing, and drying are done in the same equipment

The method of Murray and Fernberger[9] consists in employing chlorine in a solvent such as carbon tetrachloride The tin salts produced and the solvent are recovered by the addition of water or steam If desired, the solution of the tin salts in carbon tetrachloride may be electrolyzed after the addition of water

In the Acker process liquid chlorine, which continuously sets free chlorine gas, is used as a detinning agent

Sperry uses mixtures of stannic chloride and chlorine, usually in a closed system The vapors given off are cooled and condensed in chambers in the system outside of the reaction chamber

Von Kugelen and Seward, in patents assigned to the Tin Products Company of New York, use a process which depends on arranging the amount of scrap to be treated so that the heat generated by the detinning can be dissipated rapidly enough to maintain the temperature below the point at which chlorine attacks iron The stannic chloride is removed by volatilizing it in a current of chlorine In other patents Von Kugelen and Seward condense the stannic chloride in the detinning chamber They also have patented the idea of keeping that part of the detinning chamber adjacent to the walls at approximately 38° C

Leitch has patents for a process in which the scrap is detinned by chlorine while submerged in stannic chloride, the residual gas being removed by exhausting and cooling the chamber In another patent dry chlorine and stannic chloride are used alternately

Goldschmidt and Weber have a number of patents on the chlorine process under pressure, the gas acting on laminated bundles of tin scrap In some patents the gas passes from the bottom to the top, in others from the top to the bottom

Von Schutz, in all his patents and in the operation of his process, avoids pressure to as great an extent as possible, carrying on the process under suction or reduced pressure Von der Linde has patented the idea of diluting the chlorine with air by various means

The chlorine process possesses advantages over the electrolytic method, as it can be carried on in larger units, and the labor charges

[9] U S Pat 913,273 Filed Jan 17, 1906, granted Feb 23, 1909 This patent antedates that of Dubois and Kaufman, German Pat 228,952, filed May 16, 1907, granted Jan 11, 1911

are therefore materially reduced The detinning is somewhat more thorough Less tin is lost than in the competing processes The tin is recovered in the form of tin tetrachloride, which is a valuable chemical product, extensively used in the silk-dyeing industry

Practically all the corrosion problems in handling of commercial dry chlorine gas have been successfully solved Transporting and handling gaseous chlorine, while less easy than other commercial gases, is not relatively difficult

Plants for recovery of tin from tin plate scrap are fairly simple but need to be designed with due regard to many important details The plant cost per ton of scrap will vary considerably with the size of the plant

Tin plate scrap has no market as such, on the other hand detinned scrap has a ready sale Stannic-chloride crystals are in constant demand, salable at an attractive price If the manufacturer desires, tin metal can be recovered from the stannic chloride, with a good margin of profit on the tin recovery from the original scrap, but not as large as if the stannic-chloride crystals are disposed of as such

The cost of handling a ton of tin scrap in process, including all labor, interest, taxes, depreciation, materials (as chlorine), repair, and maintenance is just about equal to the amount obtained per ton of detinned scrap when it is sold as baled scrap on the open market This cost of handling does not include the nominal cost of the original tin plate scrap The values obtained then for the stannic chloride produced (or the tin recovered from such) are on the profit side of the ledger

There will be consumed approximately 80 to 100 pounds of chlorine per ton of tin plate, of the quality and weight of tin coating on tin plate commonly used for tin cans There are manufactured for food products alone in the United States enough tin plate containers so that each one of us is responsible for the consumption of at least one can per day for every day in the year The amount of scrap resulting from the fabrication of these containers is tremendous With increasing prices of tin, recovery of tin becomes of greater and more pressing importance Chlorine detinning in the United States outbids all competing processes to aid in the utilization of the huge amounts of tin plate scrap which would otherwise be a total loss and a great economic waste

CHAPTER 18

ANALYTICAL METHODS

When stannous salts are treated with hydrochloric acid, no precipitation occurs. Concentrated solutions of stannic salts become turbid in aqueous solution, owing to oxidation and hydrolysis. The formation of basic salts in this manner can be prevented by hydrochloric acid, and the oxidation may be eliminated by keeping the solution in contact with granulated tin. Stannic salts such as the chloride are hydrolyzed by water according to the reaction

$$SnCl_4 + 4H_2O = 4HCl + Sn(OH)_4$$
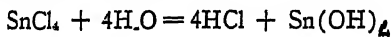
In very dilute solutions, sulfuric acid may precipitate a basic sulfate from stannic chloride.

The stannous salts are all colorless. The soluble ones yield solutions in water which have an acid reaction. All of the salts readily absorb oxygen, with the formation of stannic compounds. Alkalies, such as sodium, potassium, or ammonium hydroxide, or sodium carbonate give white precipitates of stannous hydroxide which is readily soluble in excess sodium hydroxide with the formation of sodium stannite. The precipitate also dissolves in mineral acids such as hydrochloric acid. From solutions containing not more than 2.5 per cent of concentrated hydrochloric acid, hydrogen sulfide throws down a precipitate of brown stannous sulfide. This material is soluble in strong hydrochloric acid, which distinguishes it from the sulfides of arsenic. It is nearly insoluble in colorless ammonium sulfide, which distinguishes it from the sulfides of antimony, arsenic, and stannic tin. It is soluble, however, in hot ammonium polysulfide, with the formation of ammonium thiostannate, from which hydrochloric acid precipitates yellow stannic sulfide, SnS_2. The reaction, according to Curtman,[1] is

$$SnS + (NH_4)_2S_x = (NH_4)_2SnS_3 + (x-2)S$$
$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S$$
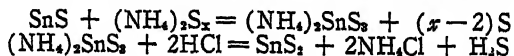
When mercuric chloride is added in excess to a solution of stannous chloride, it is reduced to white insoluble calomel, HgCl, the stannous

[1] Baskerville and Curtman, "Qualitative Analysis," New York, Macmillan, 1918.

chloride at the same time being oxidized to the stannic salt If the stannous chloride is present in excess, the calomel first formed is further reduced to gray or black metallic mercury Stannic salts do not give this reaction Bismuth salts in solution are reduced by alkali stannites Metallic zinc, or other metals higher in the electrochemical scale than tin, precipitates the metal as a gray, spongy mass when introduced into a hydrochloric-acid solution of either stannous or stannic chloride

Alkalies give a white precipitate of stannic hydroxide, $Sn(OH)_4$, which on drying becomes H_2SnO_3, as a result of their action on stannic salts in solution From moderately acid solutions of stannic salts containing not more than 2 5 per cent of concentrated hydrochloric acid, hydrogen sulfide precipitates yellow SnS_2, or stannic sulfide The sulfide is readily soluble in hydrochloric acid of one part acid to one part water Stannic sulfide readily dissolves in colorless ammonium sulfide, which distinguishes it from stannous sulfide, with formation of ammonium thiostannate, from which solution hydrochloric acid reprecipitates the sulfide When strongly ignited in air, stannic sulfide is quantitatively converted to stannic oxide

Mercuric chloride gives no precipitate with stannic salts, nor does hydrochloric or sulfuric acid when they are moderately concentrated If solutions of stannic salts are boiled, a more rapid hydrolysis occurs with the formation of a precipitate of stannic hydroxide, $Sn(OH)_4$ In the cold, potassium or sodium sulfate does not yield precipitates with stannic salts, but upon boiling, insoluble stannic hydroxide is formed

Stannic compounds occur in two forms, the normal and the metastannic variety The first may be considered as derived from stannic hydroxide formed by the action of alkalies on stannic chloride It is readily soluble in acids The metastannic compounds are derived from the white substance obtained by the action of hot dilute nitric acid on metallic tin and termed metastannic acid Its empirical formula is the same as the partially dehydrated stannic hydroxide, that is H_2SnO_3, with the distinction, however, that it is insoluble in acids When metastannic acid is boiled for a short time with concentrated hydrochloric acid, a compound of the formula $Sn_5O_5Cl_2(OH)_8$ forms, which is readily soluble in water although quite insoluble in hydrochloric acid From these reactions and the fact that similar compounds may be formed from metastannic acid, the formula $Sn_5O_5(OH)_{10}$, or $5(H_2SnO_3)$, has been assigned to it Metastannic acid is thus seen to be a polymer of stannic hydroxide The reactions of metastannic chloride,

$Sn_5O_5Cl_2(OH)_8$, are of considerable analytical interest The substance
is precipitated out of aqueous solution by hydrochloric acid, and pro-
longed boiling of the aqueous solution causes the precipitation of all
the tin as metastannic acid, which is insoluble in dilute acids Sulfuric
acid or sulfates precipitate a white substance which changes on wash-
ing with water to metastannic acid, which reaction is distinctly different
from the analogous one occurring with stannic chloride Sodium or
potassium hydroxide precipitates metastannic acid which is soluble in
excess of the reagent, but ammonium hydroxide precipitates metastannic
acid which is not soluble in excess ammonia Hydrogen sulfide forms
stannic sulfides Solutions of stannic compounds are converted into the
metastannic form by diluting and boiling, and conversely, metastannic
compounds are converted into the stannic form by boiling with con-
centrated hydrochloric acid or concentrated alkalies

A solution of a stannous salt added to a solution of auric chloride
gives a separation which is brown by transmitted light and bluish-green
by reflected light, as the result of the formation of colloidal gold, also
known as "purple of Cassius ' Stannous salts give white precipitates
when treated with either ferro- or ferri-cyanides in aqueous solutions,
while stannic salts give a white turbidity with soluble ferrocyanides,
which turbidity changes to a yellow gelatinous precipitate insoluble in
hydrochloric acid The stannic salts form no precipitate with ferri-
cyanides Lowenthal[2] found that small amounts of stannous chloride
give a very sensitive reaction when added to a mixture of ferric chloride
and potassium ferricyanide, with the resulting formation of a precipi-
tate of Berlin blue Longstaff[3] found that stannous salts can be
detected to the extent of one part in a million and a half parts by the
blue coloration formed with solutions of ammonium molybdate Stan-
nous chloride gives a yellowish-white precipitate with potassium iodide,
and with excess of the reagent orange, needle-like crystals of the double
salt are formed, while stannic chloride gives a yellow precipitate
Stannous salts give a white precipitate with oxalic acid or oxalates,
but stannic salts do not Pfaff[4] found that succinic acid and alkali
benzoates give white precipitates with stannous salts, which are visible
in dilutions as low as one in ten thousand Berzelius[5] found that stannic
salts are completely precipitated by ammonium succinate

In recent years there has been a large amount of work on tin analysis
employing organic reagents

[2] *J prakt Chem*, (1), 60 267 (1853), (1), 77 321 (1859)
[3] *Chem News*, 80 282 (1899)
[4] "Handbuch der analytischen Chemie," Altona, 1822, vol 2, p 337
[5] *Ann chim Phys*, (1), 94 187 (1815)

Quantitative Analysis of Tin Ore by Fire Assay and Volumetric Methods

The following quantitative analytical methods for tin are those of Hallett [6]

There are two general methods in use for determining the amount of tin in ores and other products, the fire assay and the volumetric wet analysis

The fire assay for tin is usually conducted in the following manner Grind slightly more than 5 grams of the sample until it will pass through a 100-mesh screen Dry at 100° C, cool, and weigh out exactly 5 grams into an 8-oz wide-mouth flask Add 100 cc hydrochloric acid (concentrated) and digest at a low heat until the volume is reduced to about 15 cc Add 50 cc nitric acid (concentrated) and continue the evaporation to a volume of 10 to 15 cc Add about 200 cc of water, boil, and allow to stand Filter on double filter papers containing paper pulp, washing with warm water just acid with nitric acid If tungsten is present, treat with ammonia (concentrated) and again filter and wash with water Transfer the precipitate to a porcelain crucible and ignite Brush the contents of the crucible onto a clean sheet of glazed paper, break up lumps with a spatula mix thoroughly with 20 grams of sodium cyanide (free from chlorides), and transfer to a 20-gram clay crucible in which has been placed 4 or 5 grams of sodium cyanide Cover with sodium cyanide, fuse in a muffle furnace at a red heat for from 20 to 25 minutes, cool, wash with water, break crucible to obtain the button, clean the button, and soak in hot water to remove adhering cyanide Dry and weigh Run in duplicate Duplicates should agree within 0 15 per cent

The volumetric determination of tin is very useful and is applicable to nearly all kinds of ores, metallurgical products, and other materials containing tin A number of volumetric methods have been proposed, the best of which depends on the titration of stannous chloride with standard iodine in cold hydrochloric acid solution This is called the Pearce-Lowe method,[7] and is one of the simplest, shortest, and most accurate for the volumetric estimation of tin It depends on the oxidation of stannous to stannic chloride by iodine in cold hydrochloric acid solution according to the equation

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI$$
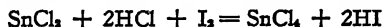
Starch solution is used as indicator A small amount of sulfuric acid is not objectionable, but nitric acid and nitrates must not be present

The method requires that the tin shall be brought into solution in hydrochloric acid When possible, the finely ground sample is dissolved directly in hydrochloric acid, in some cases the addition of a small quantity of potassium chlorate, antimony chloride, or platinic chloride, or the presence of a piece of platinum foil, accelerates solution In the analysis of materials containing sulfides or certain alloys, a mixture of hydrochloric and nitric acids may be used, followed by treatment with sulfuric acid and then with hydrochloric acid Siliceous products frequently respond to treatment with hydrofluoric acid

For the decomposition of insoluble silicates, fusion with alkali carbonates is effective Practically all silicates are decomposed by this process, but it is not suitable for use with samples containing insoluble tin oxide, and if sulfides or salts of tin soluble in acids are present they should be removed before the fusion process is applied The addition of 10 per cent of borax to the alkali carbonate accelerates the decomposition in some instances

[6] Tin chapter in Liddell, "Handbook of Non Ferrous Metallurgy," New York, McGraw Hill Book Company, Inc , 1926, pp 1389 1392
[7] *J Soc Chem Ind* , 35 1088 (1916), also Mellor, "Treatise on Quantitative Inorganic Analysis," London, Chas Griffin & Co , Ltd , 1913, p 311

Acid-insoluble residues may be decomposed by fusion with sodium or potassium hydroxide, the melt being subsequently dissolved in hydrochloric acid. This method is perhaps the most useful of the fusion processes, since it is applicable to almost all products and generally requires only a very simple preliminary acid treatment. An iron crucible is the most suitable for use with this process.

Sodium peroxide may also be used for the fusion process, but it corrodes the crucibles very rapidly, and generally its disadvantages more than offset the extra speed gained by its use. The addition of organic matter to the peroxide, to furnish the necessary heat for the reaction, has been suggested as a means of preventing the corrosion. Quieter fusion results if zinc sulfide, iron sulfide, or potassium persulfate is added to the peroxide.

In the final hydrochloric acid solution, the tin will usually be found in the stannic condition and must be reduced to the stannous condition before titration. This reduction is usually accomplished in one of four ways: by the use of iron in the form of rods, nickel or aluminum in the form of sheets or strips, or finely powdered antimony. Only pure soft iron may be used. If carbon is present in the iron, it will generally cause high results.

The use of aluminum renders this part of the method somewhat uncertain and makes it difficult to control the operation. The principal objection to the use of antimony is that the presence of so much finely powdered material in the solution obscures the end point. The only objection to nickel is the light-green color given the solution, but this does not affect the sensitiveness of the end point if the concentration of nickel salts is only that derived from the metal used for the reduction.

The reduction and the titration are best performed in an atmosphere of carbon dioxide and in a solution containing not less than 25 per cent nor more than 40 per cent by volume of free concentrated hydrochloric acid. The temperature of the solution to be titrated should not exceed 22° C.

One-half to 2 grams of the sample (depending on the percentage of tin) is first brought into hydrochloric acid solution. The solution is transferred to a 12-ounce wide-mouth conical flask, enough concentrated hydrochloric acid is added to make a total of 50 cc. of free concentrated hydrochloric acid present, and the solution is diluted to 200 cc. with water. A nickel coil is prepared by rolling 6 sq. in. of heavy sheet nickel (4 in. long and 1½ in. wide) into a loose roll of such size that it may be easily inserted into the flask. A narrow strip of nickel is left attached to one side of the coil, long enough to reach above the top of the flask. This coil is placed in the flask containing the tin solution, the nickel strip is bent over the edge, and the flask is covered with a small watch glass. The solution is heated to boiling and gentle ebullition is maintained for 30 minutes after all the iron, which is present, is reduced. The reduction of the iron is indicated by the yellow color of the solution changing to a pale green. Thirty minutes is more time than is necessary for the complete reduction of the stannic chloride from 0.5 gram of tin oxide, and if complete reduction does not result in that length of time, either the nickel coil is too small or the nickel is inactive due to impurities and should be discarded and replaced by pure nickel.

It has been stated as an objection to this method, that it is impossible to tell when the reduction of the tin is complete and that the operator may titrate the solution before the tin is all in the lower form. It has been found that larger amounts of tin than would ever be taken as a sample are entirely reduced long before the expiration of the time allowed for the reduction, and no trouble need be anticipated from this cause.

The solution in the flask is cooled in an atmosphere of carbon dioxide generated by adding two ½-inch cubes of crystalline marble to the solution. The nickel coil is then removed and is washed with cold hydrochloric acid solution (1 part of concentrated acid to 3 parts of water) as it is withdrawn from the flask. A small amount of starch solution is then added and the solution titrated at once with standard iodine.

The standard iodine solution most convenient for this titration is prepared by dissolving 10.7 grams of iodine in 50 cc. of water containing 20 grams of potassium iodide in solution and making up to 1 liter with water. When a half-gram

sample is taken for analysis, 1 cc of this solution will equal 1 per cent of tin It may be standardized against tin or arsenious oxide

Few of the elements which are ordinarily found in materials to be analyzed for tin interfere with this method Ni, Co, Mn, Mo, Ur, Cr, Al, Zn, Pb, Ca, Mg, sulfates, phosphates, bromides, iodides, and fluorides have no effect unless present in such large amount that their color masks that of the indicator Arsenious and antimonious compounds in weak acid solution consume iodine but in a hydrochloric acid solution of the strength used in this method they have no effect

If about 0 1 gram or more of antimony is present in the solution, the nickel coil will precipitate metallic antimony in a very slimy condition which does not settle and obscures the end point This may be prevented by using a solution containing more hydrochloric acid If, therefore, the sample taken contains 0 1 gram or more of antimony, the solution is made up to contain 75 cc of free concentrated hydrochloric acid instead of 50 in 200 cc of volume, before reduction If this is done, the precipitation of slimy antimony will be prevented and no trouble will be experienced If the antimony content is not known and the slimy antimony begins to precipitate during the reduction, an additional 25 cc of concentrated hydrochloric acid may be added, which will generally cause the antimony to dissolve and prevent further precipitation If the precipitated antimony does not dissolve, another sample can be treated, adding more hydrochloric acid before reduction

Copper in small amounts has no effect on the method, but if 0 05 gram or more are present in the solution it will be incompletely precipitated during the reduction, the titration will consume more iodine than is required by the tin, cuprous iodide will be precipitated, and the results will be erratic and high

If copper is present in the sample in large enough amount to interfere, it must first be removed by treatment with nitric acid

Bismuth is precipitated in the metallic form during the reduction with nickel In this form it is said to consume iodine slowly, but the action is slight, and, unless present in large amount, its effect is negligible If it is desired to remove it, the metallic precipitate may be filtered and the filtrate again reduced and finished as usual

Tungsten is reduced by the nickel coil to a lower state of oxidation, with the formation of a blue precipitate, said to be W_2O_5 This is said to be slowly oxidized by iodine, thus giving high results, but the oxidation is not proportional to the amount of tungsten present Tungsten in amounts usually met with does not interfere to any extent, and its effect is only noticeable when it is present in large quantity In case it should be desirable to separate the tungsten, the blue oxide may be filtered off with the precipitated bismuth, the solution afterwards being again reduced and titrated

Titanic chloride is reduced to titanous chloride by the nickel coil In the Pearce-Lowe method titanium alone or with iron is said to consume no iodine, but in the presence of tin large amounts of titanium will consume iodine, giving high results The error caused by titanium seems to be approximately a constant one and is independent of the amount of titanium present Titanium may best be removed by converting the tin to insoluble oxide by evaporation with nitric acid and then fusing for 5 minutes with potassium bisulfate The melt is dissolved in water and sulfuric acid and filtered

If titanium and tungsten are both present, the tungsten will remain with the tin after filtering the extracted melt of the bisulfate fusion The tungsten may be removed from this residue by heating with ammonium carbonate solution, in which the tin is insoluble

Neither bismuth, tungsten, nor titanium, in any reasonable amount, such as is usually met with, interferes with the method, and they may, in general, be neglected, especially if the titration is performed rapidly, which to a large extent will eliminate secondary reactions The interference of all of these metals is greatly increased by very slow and careful titration, which seems to accelerate their action and give them time seriously to affect the results This is especially true of titanium, for bismuth and tungsten are not so active and, as a rule, need not be considered

Ferrous chloride is oxidized only by excess of iodine, and no action takes place

unless a very large amount of iodine is run in and allowed to stand Its action is very slow even then, and the presence of iron does not affect the accuracy of this method

A tin determination may be run through and results obtained by this method in about 1½ hours, and the method is accurate to about 0 1 per cent

ANALYSIS OF TIN ORE BY HYDROGEN REDUCTION

At the Penpoll tin smelter the standard method for the determination of the tin content of ores is based on the reduction by hydrogen The following is taken from an article by W H Allen, general manager of the Penpoll Tin Smelting Company, Limited [8]

Method for Clean Ores—Weigh 0 5 gram of agated ore into a porcelain crucible (platinum shape 30 mm diameter) containing 0 6 gram pure CaO Mix intimately with a brass wire rod and brush the rod with a camel's-hair brush Reduce in hydrogen for 20 minutes at a red heat over a Meker or other suitable burner The hydrogen is passed into the crucible through a Rose crucible leading tube with cover, and sufficient gas should be used to allow of a small flame of burning hydrogen to be visible round the lid Cool while the hydrogen is still passing and if the hydrogen flame persists, blow it out After cooling place the crucible in a conical beaker (400 cc), add a few drops of water to slake the lime and then 30 cc of concentrated hydrochloric acid Heat the beaker gently till all metal has dissolved Remove the crucible with a bent glass rod and wash with 5 per cent hydrochloric acid Wash the contents of the beaker into a 1000 cc flask The solution should now have a bulk of about 100 cc

Now add 2 5 grams of pure aluminum ribbon and lay the flask on its side in water until action has almost ceased (about half an hour) The sponge of reduced tin and remaining aluminum are then redissolved by adding 40 cc concentrated hydrochloric acid and boiling on a hot plate

During boiling, the neck of the flask is closed by a rubber bung carrying a short tube with a bulb blown in it above the bung, and the lower end cut off obliquely The upper end of the tube is slightly drawn out On completion of solution the flask is connected to a carbon dioxide apparatus, by slipping the delivery tube from the latter over the drawn-out tube in the bung of the flask, at the same instant removing the flask from the hot plate This ensures the flask being filled with carbon dioxide Cool in a water trough

Standardize the iodine solution with 0 5 gram of pure tin dissolved and treated with aluminum ribbon as above Titrate the assay solution with the standard solution, using a few cc of the starch solution as indicator If the standard solution is made according to the directions given, about 61 5 cc = 0 5 gram tin

Standard Solution —

> 700 grams iodine
> 28 lbs potassium iodide
> 40 liters water

(This concentration of iodide is used so as to inhibit the effect of titanium, which interferes when less iodide is used)

Starch Indicator —Mix 5 grams of potato starch with a little cold water, add 70 cc boiling water, boil for a minute, and pour into a solution of zinc chloride in 20 cc water and 40 cc hydrochloric acid

Treatment of Ores Containing Tungsten and/or Antimony, Bismuth, Copper, and Arsenic —These elements interfere with the assay and must be removed before titration The ore is treated as before up to the stage where the metal is dissolved after the hydrogen reduction

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[8] *Mining Mag*, 40 25 (1929)

The ciucible is removed as before, but is washed with 50 per cent hydrochloric acid instead of 5 per cent A little potassium chlorate is added to the solution to oxidize and dissolve the antimony The solution is cooled, and 30 cc of cold water added This gives an acid strength of 50 per cent One gram of reduced iron is added and the solution allowed to stand 20 to 30 minutes This removes tungsten, antimony, bismuth, arsenic, and copper from solution

The iron must be free from sulfur, and the ordinary ferrum reductum is not satisfactory Merck's iron reduced by hydrogen is guaranteed free from sulfur and is the only satisfactory brand for this purpose

The solution is then filtered into the flask through a 9 cm (C S and S No 597) paper The beaker is washed twice, and the paper three times with 5 per cent hydrochloric acid In cases where much antimony is present, the precipitate is washed only once on the paper, and is then washed back into the beaker, dissolved in hydrochloric acid and a little potassium chlorate, and reprecipitated The solution is then treated with aluminum as before

Space is not available for a complete discussion of the difficult determinations involved in the analyses of pig tin and tin-bearing metals, particularly for small amounts of impurities Readers interested in this important phase of tin metallurgy are referred to the methods given in the excellent paper by William A Cowan on the metallurgy of tin and antimony, in the *J Am Inst Metals*, 8 196-229 (1914) This paper is a report of the composite work of the technicians and analysts in the laboratories of the major consumers of tin in the United States

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